

Review

In-Situ Synthesis of ZrB_2 -SiC Composite Powders: A Review of Processing-Sintering Relationships

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Abstract

Zirconium diboride-silicon carbide (ZrB_2 -SiC) composites are leading candidates for ultra-high temperature applications due to their exceptional thermal, mechanical, and oxidation resistance properties. This review critically analyzes *in-situ* synthesis strategies – namely boro/carbothermal reduction, self-propagating high-temperature synthesis (SHS), sol-gel, and polymer-derived ceramic (PDC) routes – and their impact on powder morphology, phase homogeneity, and sintering behavior. Each method presents a distinct trade-off between scalability, purity, and nanostructural control. The subsequent consolidation techniques, including hot pressing, spark plasma sintering (SPS), and pressureless sintering, are evaluated in terms of their ability to preserve the fine features of the synthesized powders. Particular attention is paid to the influence of sintering aids, grain growth inhibitors, and reactive sintering in achieving dense, defect-free microstructures. The review highlights how synthesis-sintering integration, particularly leveraging rapid consolidation techniques, governs critical performance metrics such as maximum reported hardness (up to 23 GPa) and fracture toughness (exceeding $6 \text{ MPa}\cdot\text{m}^{1/2}$). Specifically, these benchmark properties, for instance, a hardness of $22.7 \pm 1.4 \text{ GPa}$ and a fracture toughness of $6.3 \pm 0.3 \text{ MPa}\cdot\text{m}^{1/2}$, are achieved with highly integrated processes such as Reactive Spark Plasma Sintering (R-SPS) of $\text{ZrC/B}_4\text{C/Si}$ precursors, which optimizes phase homogeneity and microstructural refinement for superior performance, and oxidation behavior above 1500°C . Key microstructural determinants – such as SiC distribution and residual porosity – are discussed in relation to crack deflection, thermal shock resistance, and borosilicate glass layer formation. The work concludes by identifying the main scientific and technological barriers to industrial adoption, notably oxygen contamination, agglomeration, and process scalability, and proposes future research pathways to enable the next generation of UHTC systems.

Keywords: Nanostructure control, densification techniques, phase purity, thermal degradation, fracture mechanics

I. Introduction

Zirconium diboride-silicon carbide (ZrB_2 -SiC) composites are a foundational material class within the field of Ultra-High Temperature Ceramics (UHTCs), engineered for service in some of the most extreme thermal, mechanical, and chemical environments conceivable¹. The relentless pursuit of advanced aerospace technologies, particularly hypersonic flight vehicles, atmospheric re-entry systems, and rocket propulsion components, has created an imperative for materials that can maintain structural integrity at temperatures exceeding 2000°C ². These applications demand a unique and challenging combination of properties, including exceptionally high melting points, superior hardness and strength at elevated temperatures, high thermal conductivity to mitigate thermal shock, and robust resistance to oxidation and ablation³. Monolithic zirconium diboride (ZrB_2) possesses many of these requisite attributes, such as a melting point of approx-

imately 3245°C and high hardness⁴. However, its practical application is severely hindered by two intrinsic limitations: poor sinterability due to strong covalent bonding and low self-diffusion coefficients^{5,6}, and catastrophic oxidation at temperatures above 1200°C , where the protective boron oxide (B_2O_3) layer becomes volatile.

The incorporation of silicon carbide (SiC) into the ZrB_2 matrix is a cornerstone strategy developed to overcome these deficiencies. The addition of SiC serves a multifaceted purpose: it enhances oxidation resistance through the *in-situ* formation of a stable, viscous borosilicate glass layer that seals the porous zirconia (ZrO_2) scale; it improves sinterability and microstructural refinement by inhibiting grain growth of the ZrB_2 matrix; and it contributes to superior mechanical properties, including strength and fracture toughness⁷. The conventional method for producing these composites involves the mechanical mixing of pre-synthesized ZrB_2 and SiC powders, typically by means of ball milling. While straightforward, this approach frequently leads to inhomogeneous phase distribution,

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particle agglomeration, and the introduction of impurities from milling media, all of which can act as critical flaws that compromise the performance and reliability of the final sintered component⁸.

This review advances the central thesis that *in-situ* synthesis methods, wherein the ZrB₂ and SiC phases are formed concurrently from molecular or fine-particle precursors within a single, integrated process, offer a superior pathway to high-performance composites. By generating the constituent phases in intimate contact, these techniques can achieve a level of chemical homogeneity, microstructural refinement, and interfacial purity that is largely unattainable with mechanical mixing. This intrinsic control over the powder's fundamental characteristics is paramount, as the properties of the initial powder dictate its subsequent behavior during consolidation and ultimately determine the performance envelope of the final ceramic. The intimate relationship between the initial powder synthesis and the final bulk properties forms the critical linkage that this review seeks to elucidate. The primary objectives of this review are therefore threefold: first, to provide a critical and comparative analysis of the principal *in-situ* synthesis routes for producing ZrB₂-SiC composite powders, including solid-state reactions, combustion synthesis, and advanced chemical methods. Second, to systematically examine the crucial relationships between the distinct characteristics of these *in-situ* synthesized powders such as particle size, morphology, purity, and homogeneity – and their consolidation behavior during subsequent sintering via techniques like hot pressing, spark plasma sintering, and pressureless sintering. Third, to establish clear, evidence-based causal links between the complete processing pathway (synthesis and sintering) and the resulting microstructure, mechanical properties, and high-temperature performance of the bulk composite. This review proceeded by first evaluating the synthesis methodologies, followed by an analysis of sintering and consolidation techniques. Subsequently, it correlated these processing stages with the final microstructural and performance characteristics of the composites. The review concluded with a summary of the current state-of-the-art, a discussion of unresolved challenges, and an outlook on future research directions poised to advance this critical class of materials.

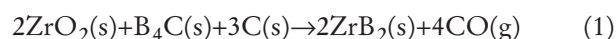
II. A Critical Evaluation of In-Situ Synthesis Routes for ZrB₂-SiC Powders

The selection of a synthesis route is the most fundamental decision in the processing of ZrB₂-SiC composites, as it predetermines the intrinsic characteristics of the starting powder and thereby sets the upper limit for the performance of the final material. A fundamental trade-off exists between process scalability and cost on one hand, and the degree of microstructural control on the other⁹. Solid-state routes are generally more scalable but offer less control, while chemical routes provide excellent control at the expense of complexity and cost. This section critically evaluates the primary *in-situ* synthesis methodologies, focusing on their reaction mechanisms, process

control variables, and the unique characteristics of the resultant composite powders. A comparative summary of the four primary *in-situ* synthesis routes – boro/carbothermal reduction, SHS, sol-gel synthesis, and the PDC route – is provided in Table 1, highlighting their key process parameters, advantages, limitations, and typical powder characteristics.

(1) Solid-State Boro/Carbothermal Reduction

The boro/carbothermal reduction of metal oxides is the most established and widely investigated solid-state route for the synthesis of ZrB₂-SiC composite powders, valued for its use of relatively inexpensive and abundant precursors¹⁴. The fundamental principle involves the high-temperature reduction of a zirconium source, typically zirconia (ZrO₂) or zircon (ZrSiO₄), in the presence of boron and carbon sources. A common reaction system involves the reduction of ZrO₂ using boron carbide (B₄C) as the boron source and elemental silicon (Si) and/or free carbon (C) as the reductants and SiC formers. A representative reaction is given by Equation (1)¹⁰:



When elemental silicon is included to form the SiC phase *in-situ*, the reaction stoichiometry can be adjusted accordingly. Thermodynamic analyses confirm the feasibility of these reactions, typically predicting onset temperatures above 1200 °C, with the evolution of carbon monoxide (CO) gas as a significant byproduct that helps drive the reaction to completion. An economically attractive variant utilizes zircon sand (ZrSiO₄) as the zirconium and silicon source, which reacts with B₄C and C, although this often requires higher temperatures for the initial decomposition of the stable zircon silicate⁸. Control over the final powder characteristics is achieved through careful manipulation of several process parameters. The reaction temperature and holding time are the most critical variables, directly influencing the degree of reaction completion and the extent of particle coarsening and agglomeration; temperatures are typically in the range of 1400–1600 °C for several hours¹⁵. The choice of precursors has a marked effect on the final microstructure. For instance, Jyoti *et al.*¹⁰ demonstrated that using amorphous carbon black as the carbon source and elemental silicon as the silicon source resulted in a finer, impurity-controlled ZrB₂-SiC composite at 1500 °C, compared to using graphite and silicon, which required 1600 °C. The stoichiometry of the reactants is also crucial for achieving phase purity. Cao *et al.*⁸, investigating the synthesis from ZrSiO₄, found that an excess of boric acid (20–30 wt%) was necessary to compensate for its volatility and ensure the complete conversion of intermediate phases to obtain high-purity ZrB₂-SiC powders at 1650 °C. Furthermore, the morphology of the product can be tailored. While equiaxed particles are common, the introduction of catalysts like iron in a molten salt medium has been shown to promote the *in-situ* growth of SiC whiskers with high aspect ratios, which are desirable for enhancing fracture toughness¹⁶. The presence of the

Table 1: Comparative analysis of *in-situ* synthesis routes for ZrB₂-SiC powders.

Synthesis Route	Typical Precursors	Reaction Temperature (°C)	Key Process Characteristics	Advantages	Disadvantages/Challenges	Typical Powder Characteristics	Context/Notes	References
Boro/carbothermal reduction	ZrO ₂ , B ₄ C, C, Si; ZrSiO ₄ , B ₄ C, C	1 400 – 1 650	Solid-state diffusion-controlled reaction; long holding times (hours)	Low-cost precursors; scalable; relatively simple process	High temperatures; coarse, agglomerated powders; low sintering activity; potential for incomplete reaction and impurities (ZrO ₂ , C)	Micron to sub-micron sized particles; often irregular or equiaxed morphology; purity depends on conversion	Achieved at high temperature (1 650 °C), demonstrating optimal reduction kinetics.	10
SHS	ZrO ₂ , Mg, B ₂ O ₃ , Si; Zr, B ₄ C, Si	> 1 800 (transient)	Rapid, self-sustaining exothermic reaction; combustion wave propagation	Highly energy efficient; very rapid process (minutes); potential for high purity	Difficult to control; can lead to molten or heavily sintered product; inhomogeneous microstructure; incomplete conversion	Sub-micron to micron-sized particles; often sintered agglomerates; purity can be high	Achieved via water-washing (BRW) refinement, corresponding to high oxygen retention (~ 1.98 wt%).	11
Sol-gel synthesis	Zr(OPr) ₄ , TEOS, H ₃ BO ₃ , Sucrose/Glucose	1 300 – 1 500 (pyrolysis)	Molecular-level mixing in liquid phase; formation of homogeneous precursor gel	Ultra-fine/nano-sized powders; high homogeneity and purity; high sintering activity	Expensive precursors; complex multi-step process; low ceramic yield; significant shrinkage; difficult to scale up	Nanoparticles (< 200nm); equiaxed/spherical; high specific surface area	Superior purity attained due to molecular-level precursor mixing.	12
PDC	Polycarbosilane, Cp ₂ ZrCl ₂ , TEAB	1 400 – 1 800 (pyrolysis)	Synthesis of a single-source preceramic polymer followed by pyrolysis	Unprecedented nanostructural control; ability to form fibers/coatings; true nanocomposites	Very complex precursor synthesis; expensive and air-sensitive precursors; difficult stoichiometry control; scalability is a major hurdle	Nanocomposite particles (e.g., ZrB ₂ nano-inclusions in SiC matrix); morphology dictated by polymer architecture	Consistent particle refinement enhanced by uniform SiC dispersion.	13

SiC phase itself plays a crucial role in microstructural development, acting as a grain growth inhibitor for ZrB₂ particles during synthesis via a pinning effect, leading to a finer composite powder than would be obtained for monolithic ZrB₂ under similar conditions¹⁰. Fig. 1 illustrates the conceptual difference between powders produced by conventional mechanical mixing versus a homogeneous *in-situ* synthesis route.

Despite its widespread use, the boro/carbothermal reduction method presents a classic trade-off. Its primary advantages are its operational simplicity, potential for scalability, and reliance on low-cost oxide and carbide precursors. However, the method is beset by significant challenges. The high temperatures and long reaction times required to overcome solid-state diffusion limitations invariably lead to coarse, heavily agglomerated powders

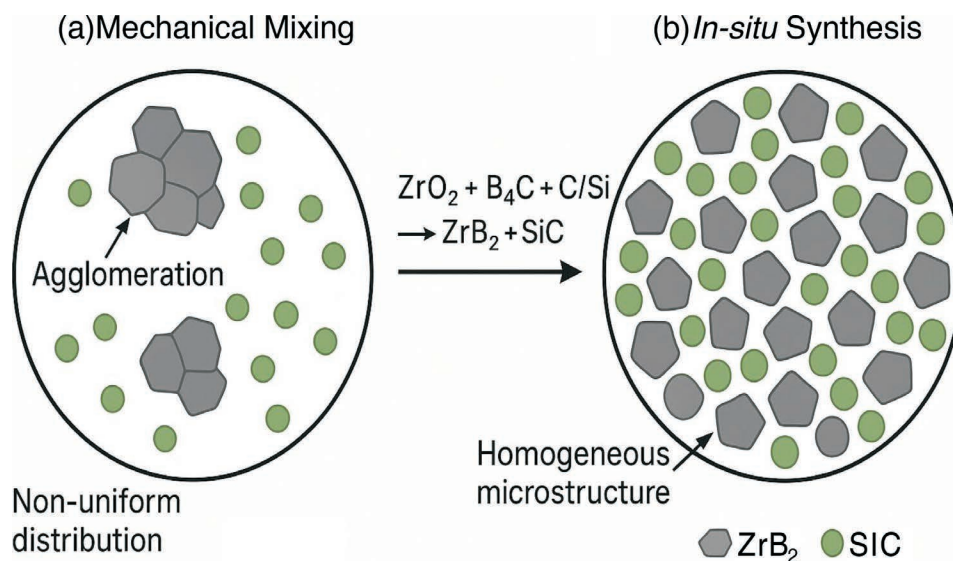


Fig. 1: Conceptual schematic illustrating the critical microstructural differences achieved by powder processing routes. (a) Conventional mechanical mixing. (b) *In-situ* synthesis.

with low specific surface area and consequently poor sintering activity¹⁵. Incomplete reactions are a common problem, resulting in residual impurities such as unreacted ZrO_2 or free carbon, which can degrade the mechanical and thermal properties of the final sintered ceramic⁸. Achieving nanoscale homogeneity is inherently difficult, as the process relies on diffusion between discrete solid particles rather than mixing at a molecular level.

(2) Self-propagating high-temperature synthesis (SHS)

SHS, also known as combustion synthesis, is a highly energy-efficient processing technique that harnesses the heat generated by strong exothermic formation reactions to sustain the synthesis process¹⁴. Once initiated by a localized external energy source (e.g., a heated filament or laser pulse), a combustion wave propagates through the reactant compact, rapidly converting it into the final product without requiring further external energy. The viability of an SHS process is often predicted by the adiabatic temperature (T_{ad}), the theoretical maximum temperature the reaction can reach. A widely accepted empirical criterion suggests that a reaction can be self-sustaining if T_{ad} exceeds 1800 K¹⁴. Several reaction systems have been explored for the *in-situ* SHS of ZrB_2 - SiC . One approach is the magnesiothermic reduction of oxides, such as a mixture of ZrO_2 , B_2O_3 (or H_3BO_3), Si, and Mg, where the highly exothermic reaction between Mg and the oxides provides the energy to drive the synthesis¹¹. Another prominent route involves the direct reaction between more energetic precursors, such as elemental powders (Zr, Si, B, C) or carbides (ZrC , B_4C)¹⁷. For example, the reaction $2\text{Zr} + \text{B}_4\text{C} + \text{Si} \rightarrow 2\text{ZrB}_2 + \text{SiC}$ is sufficiently exothermic to be self-propagating.

Controlling the intense and rapid SHS reaction is the primary challenge and the focus of significant research. Uncontrolled reactions can lead to excessively high temperatures, causing melting, severe grain coarsening, and phase segregation in the product. A key strategy for moderating the reaction is the addition of an inert

diluent, such as sodium chloride (NaCl) or a pre-synthesized portion of the final product (ZrB_2 - SiC), to the initial reactant mixture. The diluent acts as a heat sink, absorbing some of the reaction enthalpy to lower the combustion temperature and velocity, which in turn leads to a finer and less agglomerated product powder¹¹. Another sophisticated control strategy involves the use of a metallic binder, such as nickel (Ni), in the reactant system (e.g., Ni-Zr- B_4C)¹⁸. The metal serves multiple purposes: it can form low-melting-point eutectics with the reactants (e.g., Ni-Zr or Ni-B liquids), which facilitates ignition and accelerates reaction kinetics by providing a liquid medium for diffusion. The liquid phase also helps to dissipate heat more effectively and can physically separate the growing ceramic grains, thereby inhibiting coarsening. Studies have shown that increasing the Ni content systematically decreases the combustion temperature and results in a significant refinement of the final ZrB_2 and ZrC particle size, from several microns down to the sub-micron level¹⁸. The characteristics of the precursors, such as the particle size of B_4C , also play a critical role, with finer reactants leading to easier ignition and more complete conversion. A schematic representation of the SHS process is shown in Fig. 2.

The SHS method offers compelling advantages, primarily its extreme rapidity, minimal energy consumption, and the potential to produce high-purity products, as the intense heat can vaporize volatile impurities¹¹. However, the technique's primary drawback is the inherent difficulty in controlling the process. The high thermal gradients and rapid kinetics can lead to microstructural inhomogeneity, broad particle size distributions, and residual porosity. Incomplete conversion is also a frequent issue, particularly in magnesiothermic systems where reactant loss through vaporization can occur. Khanra *et al.* developed a “double SHS” (DSHS) technique, where the product of a first SHS reaction is mixed with additional reactants and subjected to a second combustion wave to improve conversion and

further refine the particle size¹⁹. Thus, while SHS is a powerful tool for rapid synthesis, significant process engineering is required to produce powders with the controlled characteristics needed for high-performance ceramics.

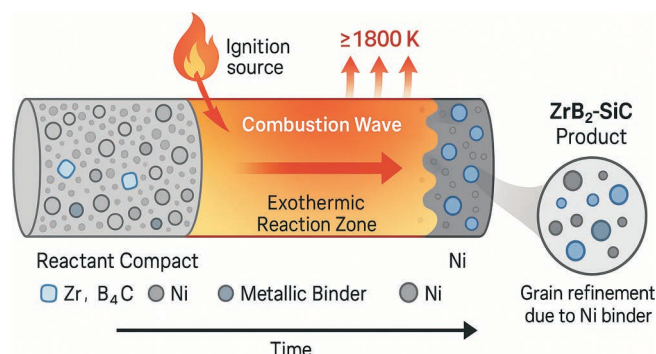


Fig. 2: Schematic diagram illustrating the SHS process for ZrB₂-SiC powder. The reaction, initiated by a localized heat source, is driven by the internal exothermic heat of formation, which sustains a combustion wave through the reactant compact.

(3) Sol-gel synthesis

In stark contrast to the high-temperature, diffusion-limited solid-state routes, sol-gel synthesis represents a “bottom-up” chemical approach that achieves unparalleled precursor mixing at the molecular level²⁰. This method begins with the preparation of a colloidal suspension (sol) of precursors in a liquid, which is then induced to form a continuous, three-dimensional solid network (gel). For ZrB₂-SiC synthesis, this typically involves the controlled hydrolysis and condensation of metal-organic precursors, such as zirconium *n*-propoxide (Zr(OPr)₄) as the zirconium source and tetraethyl orthosilicate (TEOS) as the silicon source. These are dissolved in a solvent, commonly ethanol, along with a boron source (e.g., boric acid, H₃BO₃) and a carbon source that can be incorporated into the gel network, such as a sugar (sucrose, glucose) or a polymer like phenolic

resin²⁰. The key to the process is the formation of a homogeneous gel wherein the Zr, Si, B, and C precursor species are intimately and uniformly distributed on a scale approaching the molecular. This precursor gel is then dried and subjected to a carbothermal reduction heat treatment, typically in an inert atmosphere, to convert it into the final ceramic composite powder.

The success of the sol-gel route is critically dependent on precise control over the solution chemistry and subsequent heat treatment. The hydrolysis rates of the metal alkoxides must be carefully managed to prevent precipitation and ensure the formation of a homogeneous gel. Chemical modifiers, such as acetic acid, are often employed to chelate the zirconium precursor, thereby reducing its reactivity and promoting co-condensation with the less reactive silicon precursor, ensuring a uniform distribution of elements in the final gel²¹. The choice and quantity of the carbon source are also vital. Sugars are effective as they can be dissolved and integrated into the gel, pyrolyzing to provide a highly reactive, amorphous carbon source that is finely dispersed throughout the oxide network²⁰. The molar ratios of the reactants, particularly the boron-to-zirconium ($n(B)/n(Zr)$) and carbon-to-metal ($n(C)/n(Zr+Si)$) ratios, must be optimized to ensure complete conversion and achieve phase purity in the final product¹⁵. A significant advantage of this approach is that the carbothermal reduction of the highly reactive, amorphous, and intimately mixed precursor gel can be accomplished at substantially lower temperatures (e.g., 1 300–1 500 °C) and for shorter times compared to conventional solid-state reactions²⁰.

The sol-gel method stands out because of its ability to produce composite powders with exceptional characteristics. The resulting powders are typically ultra-fine, often with crystallite sizes well below 200 nm, and exhibit high purity, a high degree of chemical homogeneity, and large specific surface areas (~ 20 m²/g)¹⁵. These properties impart excellent sintering activity, making the powders highly desirable for fabricating dense ceramics. Fig. 3 shows representative morphologies of powders

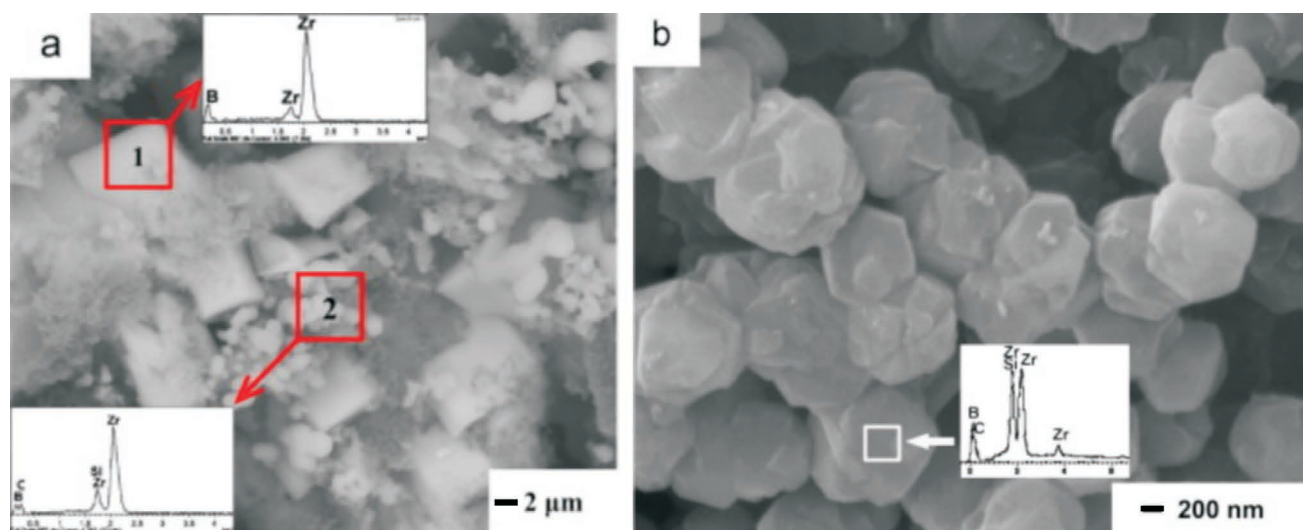


Fig. 3: Representative SEM images comparing the resultant morphology and size distribution of ZrB₂-SiC composite powders derived from distinct synthesis routes. (a) Ultra-fine nanocomposite powder. (b) Coarse and agglomerated powder¹⁵.

synthesized with different methods, highlighting the fine, equiaxed nature of sol-gel derived powders. However, the sol-gel route is not without significant drawbacks that have limited its industrial application. The process is complex and sensitive to numerous variables, including pH, temperature, and precursor concentrations, making it difficult to control and scale up²⁰. The metal-organic precursors are often expensive and air-sensitive, requiring specialized handling. Furthermore, the process is characterized by large volume shrinkage during the drying and pyrolysis steps and generally suffers from a low ceramic yield, meaning a large portion of the precursor mass is lost as volatile byproducts⁸.

(4) *Polymer-derived ceramics (PDC) route*

The PDC route represents one of the most advanced and versatile chemical synthesis strategies, leveraging the processability of polymers to create ceramic materials with unique compositions and tailored nanostructures¹³. The core of the PDC approach is the design and synthesis of a preceramic polymer – often termed a “single-source precursor” – that contains all the necessary elements (e.g., Zr, Si, B, C) chemically bonded within its molecular backbone. This polymer can be shaped in its plastic state (e.g., spun into fibers, cast into films) and is subsequently pyrolyzed in a controlled, inert atmosphere. During pyrolysis, the polymer decomposes, releasing volatile organic fragments and transforming into an amorphous or nanocrystalline ceramic material whose final composition and phase distribution are a direct reflection of the initial polymer’s molecular architecture²².

The synthesis of a suitable hybrid preceramic polymer is the most critical step in the PDC process. For the ZrB₂-SiC system, this typically involves reacting a silicon-containing polymer, such as polycarbosilane (a source of Si and C), with organometallic zirconium and boron precursors. For example, Yu *et al.*²² successfully synthesized a single-source precursor for ZrC-ZrB₂-SiC nanocomposites by reacting allylhydridopolycarbosilane (AHPCS) with bis(cyclopentadienyl) zirconium dichloride (Cp₂ZrCl₂) and triethylamine borane (TEAB). The resulting polymer, containing Si-C, Zr-C, and B-N bonds, was then pyrolyzed at temperatures up to 1 800 °C to yield the ternary ceramic nanocomposite. This route provides a level of microstructural control that is truly unique. It enables the formation of true nanocomposites where one phase is finely dispersed within another on a scale of nanometers. For instance, studies have reported the synthesis of powders consisting of highly spherical ZrB₂ nanoparticles (tens of nanometers in diameter) uniformly embedded within a continuous SiC matrix¹².

The PDC route offers unparalleled control over the final nanostructure and phase distribution, opening pathways to novel composite architectures and functionalities. The ability to process the material in a polymeric state before ceramization is a significant advantage for fabricating complex shapes such as ceramic matrix composite (CMC) fibers or coatings¹³. Furthermore, some single-source precursors have been developed that exhibit high ceramic yields (up to 85 %), which is a notable improvement

over many sol-gel systems²². However, the PDC route is arguably the most complex and least mature of the synthesis methods discussed. The synthesis of appropriate, high-yield preceramic polymers is a significant challenge in organometallic chemistry and is often costly. Controlling the final stoichiometry of the ceramic can be difficult, as different parts of the polymer may volatilize at different rates during pyrolysis. Oxygen contamination is a major concern, as many precursors are highly sensitive to air and moisture, and any oxygen incorporated into the polymer network will persist in the final ceramic as an oxide impurity. Consequently, while the PDC route holds immense scientific promise for creating next-generation materials, significant challenges in precursor synthesis, process control, and scalability must be overcome before it can be considered for widespread application.

III. Consolidation and Sintering of In-Situ Synthesized Powders

The successful synthesis of a high-quality composite powder is only the first step toward fabricating a useful engineering component²³. The subsequent consolidation of this powder into a dense, fully ceramic body is equally critical and presents its own set of challenges, particularly for covalently bonded materials like ZrB₂ and SiC. The characteristics of the powder derived from the *in-situ* synthesis route – particle size, purity, morphology, and homogeneity – have a profound and direct influence on its sinterability and the selection of an appropriate consolidation technique²⁴. A synergistic relationship exists wherein advanced synthesis routes that produce nano-structured powders are best paired with advanced sintering techniques capable of consolidating them without excessive grain growth, thus preserving the unique benefits conferred during synthesis.

(1) *The influence of powder characteristics on sinterability*

The driving force for solid-state sintering is the reduction of the system’s total surface free energy. Consequently, powders with a smaller particle size and thus a higher specific surface area possess a significantly greater driving force for densification¹⁴. This is a primary reason why powders produced via chemical routes like sol-gel or PDC, which typically have particle sizes in the nanometer range, exhibit enhanced sinterability compared to the coarser, micron-sized powders often resulting from conventional boro/carbothermal reduction or SHS¹⁴. The use of nano-sized starting powders can dramatically lower the required sintering temperature and time needed to achieve high relative densities²⁵.

Beyond particle size, powder purity plays a crucial role. The surfaces of ZrB₂ and SiC particles are often passivated by thin native oxide layers (ZrO₂, B₂O₃, SiO₂). These oxide layers act as diffusion barriers, inhibiting the formation of strong inter-particle necks and hindering densification²⁶.

In-situ synthesis methods, particularly the chemical routes, can produce powders with lower oxygen content and cleaner surfaces, thereby improving their intrinsic sintering activity. Conversely, powders from

incomplete solid-state reactions may contain residual oxide phases that impede full densification²⁷. Powder morphology^{28–30} and the degree of agglomeration^{31, 32} also impact sinterability. Hard agglomerates are difficult to break down during compaction and can lead to large, persistent pores in the final microstructure, whereas soft agglomerates of fine, equiaxed particles lead to better green body packing and more uniform shrinkage during sintering.

(2) Comparative analysis of sintering techniques

The choice of sintering technique must be matched to the characteristics of the *in-situ* synthesized powder to achieve optimal densification while controlling microstructural evolution.

Hot pressing (HP) is the traditional and most widely studied method for densifying $\text{ZrB}_2\text{-SiC}$ composites. It involves the simultaneous application of high temperature (typically $> 1900^\circ\text{C}$) and uniaxial pressure ($\approx 30\text{ MPa}$) to a powder compact within a graphite die³³. The applied pressure assists in particle rearrangement, promotes plastic flow at contact points, and enhances diffusional transport, thereby overcoming the inherently poor sinterability of these covalent materials. While effective at achieving high densities, the long dwell times, often lasting 1 to 3 hours, required for conventional HP at these high temperatures often lead to significant grain growth, which can negate the benefits of starting with a fine-grained or nano-structured powder.

Spark plasma sintering (SPS) has emerged as a transformative consolidation technology for UHTCs and other difficult-to-sinter materials. In SPS, a pulsed high-amperage, low-voltage direct current is passed directly through the graphite die and, in the case of conductive materials like $\text{ZrB}_2\text{-SiC}$, through the powder compact itself. SPS processing utilizes extremely rapid heating rates (typically $100\text{--}300\text{ K/min}$ compared to $10\text{--}20\text{ K/min}$ for

conventional HP)³⁴. The proposed mechanisms for enhanced densification include plasma generation in inter-particle voids, which cleans particle surfaces, and intense localized Joule heating at particle contacts, which accelerates diffusion³⁵. The primary advantage of SPS is its ability to consolidate nano-structured powders to full density while effectively suppressing grain growth, thereby preserving the fine microstructure created during advanced synthesis³⁴. This synergy between nano-powder synthesis and rapid consolidation is key to producing high-performance, fine-grained UHTCs.

Furthermore, SPS facilitates a processing strategy known as reactive sintering, which represents the highest level of process integration. In this approach, a mixture of precursor powders (e.g., ZrC , B_4C , and Si) is loaded into the SPS die, and the synthesis reactions to form ZrB_2 and SiC occur *in-situ* during the rapid heating cycle¹⁷. The applied pressure acts concurrently to consolidate the newly formed, highly reactive product phases into a dense body. Aguirre *et al.*³⁶ demonstrated this by reactively sintering a $\text{B}_4\text{C} + 2\text{ZrC} + 3\text{Si}$ mixture, where a diffusion reaction between B_4C and ZrC formed ZrB_2 , while liquid Si reacted with free carbon to form SiC , resulting in a dense, interpenetrating composite within minutes. This approach blurs the line between synthesis and consolidation, offering remarkable efficiency by eliminating the separate powder synthesis step and capitalizing on the high activity of nascent reaction products. Fig. 4 provides a schematic comparison of the conventional HP and advanced SPS processes.

Fig. 4: Schematic comparison of two primary consolidation techniques: (a) Conventional HP, which uses external heating and uniaxial pressure over long durations, and (b) SPS, which uses a pulsed DC current for rapid internal heating and consolidation under pressure, significantly reducing sintering time and temperature.

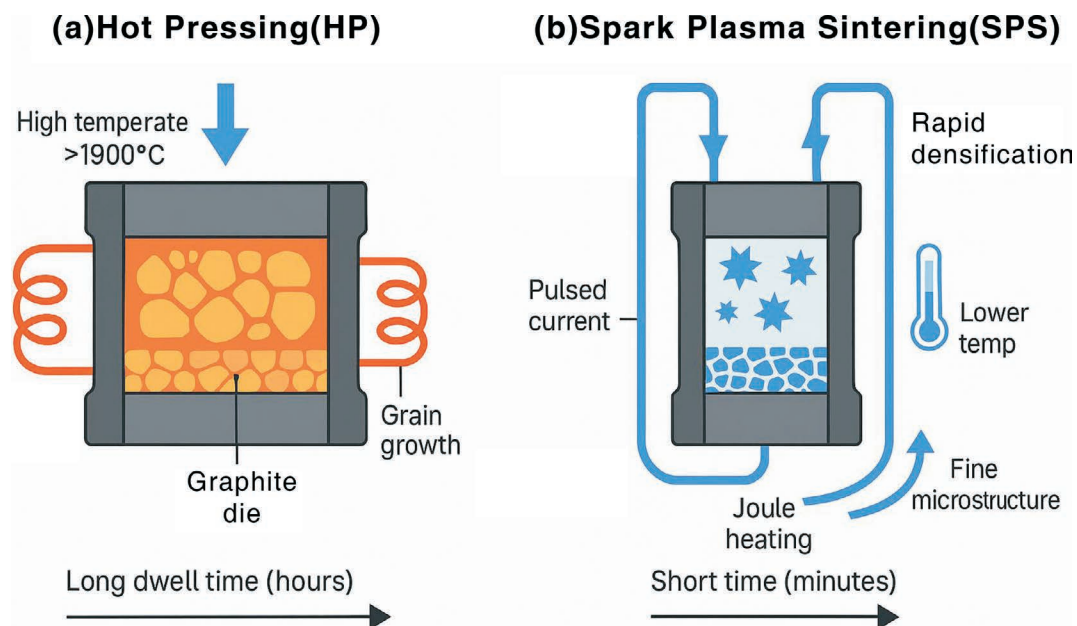


Fig. 4: Schematic comparison of two primary consolidation techniques: (a) Conventional HP, which uses external heating and uniaxial pressure over long durations, and (b) SPS, which uses a pulsed DC current for rapid internal heating and consolidation under pressure, significantly reducing sintering time and temperature.

Pressureless sintering is the most economically desirable consolidation method as it eliminates the need for expensive hot-pressing or SPS equipment. However, achieving full density in $\text{ZrB}_2\text{-SiC}$ without applied pressure is extremely challenging. Historically, it was considered nearly impossible. Recent advances, however, have demonstrated that near-full densification ($> 97\%$) can be achieved via pressureless sintering, but this success is almost entirely predicated on two factors: the use of highly sinter-active, ultra-fine, or nano-sized *in-situ* synthesized powders, and the strategic use of sintering aids³⁷. The high surface energy of the nano-powders provides the necessary driving force, while the sintering aids facilitate the material transport mechanisms required for pore elimination.

(3) The role and controversy of sintering aids

Sintering aids are often indispensable for achieving full densification in $\text{ZrB}_2\text{-SiC}$ composites, particularly in pressureless sintering and, to a lesser extent, in HP. Their role is to enhance the material transport mechanisms that lead to densification. A primary mechanism involves the removal of surface oxide impurities. Additives like B_4C and free carbon (C), often derived from the pyrolysis of a phenolic resin binder, are highly effective in this regard³⁸. At high temperatures, they react with the native ZrO_2 and SiO_2 on the powder surfaces, reducing them to the parent boride and carbide and generating gaseous byproducts (e.g., CO, SiO). This “cleans” the particle surfaces, creating high-energy interfaces that promote solid-state diffusion and neck growth⁷. Another class of additives functions by forming a transient liquid phase at the sintering temperature. Metallic additives such as nickel

(Ni), or silicides like molybdenum disilicide (MoSi_2), can form low-melting-point eutectics with the constituents of the composite⁷. This liquid phase wets the solid ceramic grains and accelerates densification through a solution-reprecipitation mechanism, which is significantly faster than solid-state diffusion.

However, the use of sintering aids is a subject of significant debate and represents a critical processing trade-off³⁹. While they are highly effective at promoting densification, they invariably introduce secondary phases into the final microstructure⁴⁰. These phases typically reside at the grain boundaries⁴¹ and can have properties, such as lower melting points or lower strength, that are inferior to the primary ZrB_2 and SiC phases⁴². The presence of these grain boundary phases can be detrimental to the composite's high-temperature mechanical properties, such as creep resistance, and can negatively impact its oxidation behavior. Therefore, a central challenge in the field is to balance the need for high density, which often requires sintering aids, against the desire for high compositional purity to maximize high-temperature performance⁴³. The ideal sintering aid would be one that is effective at promoting densification but is either completely removed from the system after sintering or forms a refractory and benign grain boundary phase.

A comparative summary of representative sintering parameters, additive strategies, and resulting mechanical properties for various *in-situ* synthesized $\text{ZrB}_2\text{-SiC}$ composites is provided in Table 2, illustrating how the interplay between synthesis route, sintering method, and aid selection governs final densification and performance outcomes.

Table 2: Representative sintering parameters and resulting properties of *in-situ* derived $\text{ZrB}_2\text{-SiC}$ composites.

Powder Synthesis Route	Sintering Method	Sintering Parameters	Sintering Aid(s)	Final Rel. Density (%)	Hardness (GPa)	Fracture Toughness ($\text{MPa}\cdot\text{m}^{1/2}$)	References
<i>In-situ</i> sol-gel/carbothermal	Pressureless sintering	2 250 °C, 2 h	B_4C , Mo	96.6	13.9 ± 0.3	-	37
Boro/carbothermal reduction	Pressureless sintering	2 100 °C	C, B_4C	> 97	14.7 ± 0.2	4.0 ± 0.5	44
Reactive precursors (Zr, Si, B_4C)	Reactive hot pressing	1 800 °C, 1 h, 20 MPa	None (reactive)	96.6	-	-	45
Reactive precursors (ZrC , B_4C , Si)	Reactive SPS	1 800 °C, 5 min, 30 MPa	None (Reactive)	> 99	22.7 ± 1.4	6.3 ± 0.3	46
Reactive precursors (B_4C , ZrC , Si)	Reactive SPS	Not specified	None (Reactive)	95	-	6.03 ± 0.45	36
Pre-synthesized nano-powders	SPS	1 600 °C, 2 min, 55 MPa	None	> 99	23.0	5.4	33
Pre-synthesized powders	HP	1 750 °C	MoSi_2	> 99	> 20	~ 5.5	47

IV. Correlating Processing with Microstructure and Performance

The ultimate goal of tailoring the synthesis and sintering processes is to engineer a composite with a specific microstructure designed to deliver optimal performance⁴⁸. The properties of ZrB₂-SiC composites are governed by a hierarchy of structural features – ranging from atomic-level purity and grain boundary chemistry to micro-scale grain size and phase distribution, and finally to macro-scale defects like pores and agglomerates – all of which are direct consequences of the processing history. This section synthesizes the preceding discussions to build a comprehensive understanding of these critical processing-microstructure-property relationships.

(1) Microstructural evolution and control

The final microstructure of a sintered ZrB₂-SiC composite is the cumulative result of the powder synthesis and consolidation steps. One of the most critical microstructural features is the grain size of the primary ZrB₂ phase. The SiC particles, particularly when finely and homogeneously dispersed by means of *in-situ* synthesis, play a crucial role as grain growth inhibitors. During sintering, the SiC particles located at the ZrB₂ grain boundaries exert a pinning force (Zener pinning), which impedes grain boundary migration and thus restricts the coarsening of the ZrB₂ grains¹⁰. This effect is essential for producing fine-grained composites, which generally exhibit superior mechanical properties. The effectiveness of this pinning is maximized when the SiC particles are small and uniformly distributed, a condition best met by powders derived from chemical synthesis routes.

The choice of sintering technique further refines the microstructure. The rapid heating and short dwell times characteristic of SPS are particularly effective at consolidating fine powders to high density while minimizing grain growth, thus preserving the nano-scale features of the initial powder³⁴. In contrast, the prolonged exposure to high temperatures during conventional HP or pressureless sintering inevitably leads to more significant grain coarsening.

Phase homogeneity is another critical attribute directly linked to the synthesis method. Chemical routes like sol-gel and PDC, which achieve molecular-level mixing, yield an exceptionally uniform distribution of the SiC phase within the ZrB₂ matrix²⁰. This uniformity is vital for ensuring consistent properties throughout the component. In contrast, powders synthesized via solid-state routes, and especially those made by conventional mechanical mixing, are prone to the formation of SiC agglomerates. These agglomerates not only lead to an inhomogeneous microstructure but can also act as large, strength-limiting defects in the final ceramic⁴⁹. Finally, the elimination of porosity and defects is a primary goal of sintering. Incomplete densification leaves residual porosity, which severely degrades mechanical strength. Similarly, impurities from the synthesis process, such as residual ZrO₂ from incomplete carbothermal reduction or secondary phases from sintering aids, often concentrate at

grain boundaries and can compromise high-temperature strength and oxidation resistance¹⁵.

The mechanical and thermal reliability of ZrB₂-SiC composites is intrinsically linked to the stability of their microstructure, specifically the control of ZrB₂ grain growth during high-temperature consolidation. The inclusion of SiC is critical not only for enhanced oxidation resistance but also as a structural stabilizer, enabling the preservation of fine grain sizes necessary for superior hardness and strength.

The primary mechanism governing this microstructural refinement is Zener pinning (or Zener drag). During sintering, the driving force for ZrB₂ grain growth arises from the reduction of total grain boundary energy, causing boundaries to migrate. When SiC second-phase particles are strategically located at the ZrB₂ grain boundaries, they exert a retarding force (F_Z) that impedes boundary motion. The maximum pinning pressure (P_Z) exerted by the particles is fundamentally governed by the Zener relationship, which dictates that P_Z is proportional to the volume fraction (f) of the second phase and inversely proportional to the radius (r) of the pinning particles. Therefore, achieving optimal grain growth inhibition requires maximizing the SiC volume fraction while minimizing its particle size.

The efficiency of SiC content in kinetic suppression has been shown to be dramatic and non-linear. Studies investigating the influence of SiC volume fraction on densification confirmed that increasing the content from 10 vol% to 30 vol% significantly enhances grain growth inhibition and improves the final relative density. This relationship is driven by a geometrical phenomenon: low concentrations of the second phase are insufficient to cover all ZrB₂ grain boundaries, leaving highly energetic, unpinning sections that can migrate rapidly. Quantitative kinetic analyses provide compelling evidence for this critical threshold effect. High-temperature heat treatments showed that the ZrB₂ grain growth rate in a ZrB₂-30 vol% SiC composite was suppressed by a factor of 25 compared to a ZrB₂-10 vol% SiC composition during equivalent thermal exposure. This extreme kinetic suppression factor underscores why higher SiC loadings (typically 20–30 vol%) are favored; the geometric increase in boundary coverage at higher fractions efficiently saturates the grain boundaries, forcing grain coarsening to proceed through the much slower processes of lattice diffusion or SiC particle Ostwald ripening, effectively halting the migration of the ZrB₂ matrix boundaries. This microstructural stability is what allows the high temperatures necessary for full ZrB₂ densification to be reached without suffering catastrophic microstructural degradation.

(2) Mechanical properties

The mechanical performance of ZrB₂-SiC composites is a direct function of the microstructure established during processing. Key properties such as hardness, strength, and fracture toughness are intimately linked to features like grain size⁵⁰, phase distribution⁵¹, and the presence of defects.

The hardness and flexural strength of ceramic materials are typically sensitive to grain size, often following the

Hall-Petch relationship, where strength increases as grain size decreases. Consequently, composites fabricated from fine-grained powders and consolidated using techniques that limit grain growth, such as SPS, consistently exhibit higher hardness and strength values⁴⁹. Hardness values for dense ZrB₂-SiC composites typically range from 18 to 25 GPa, while flexural strengths can exceed 1 000 MPa in optimized, fine-grained materials⁴⁹.

Fracture toughness, a measure of a material's resistance to crack propagation, is a critical property for structural applications. While monolithic ZrB₂ has a relatively low fracture toughness (3–4 MPa·m^{1/2}), the addition of a second phase like SiC significantly improves it, with values for dense composites typically ranging from 5 to 7 MPa·m^{1/2}. This enhancement is attributed to several toughening mechanisms that operate at the microstructural level. When a crack propagates through the ZrB₂ matrix and encounters a SiC particle, it can be deflected, forced to change its path, which consumes additional energy. The residual stresses arising from the thermal expansion mismatch between ZrB₂ and SiC can also create a compressive stress field around the SiC particles, which helps to close the crack tip. Other mechanisms include crack bridging, where intact SiC particles span the crack wake, and microcracking in the stress field ahead of the main crack tip, which dissipates energy. The effectiveness of these mechanisms is highly dependent on the size, shape, and distribution of the SiC phase. For example, composites reinforced with *in-situ* grown SiC whiskers or fibers often exhibit superior toughness due to the activation of whisker pull-out and bridging mechanisms⁵². However, the role of the SiC phase presents a complex optimization problem. While SiC is a crucial reinforcing agent, the same thermal expansion mismatch that generates beneficial residual stresses can also be detrimental if not properly controlled. There exists a critical SiC particle size, reported by Watts *et al.* to be approximately 11.5 μm, above which the stored strain energy from the thermal mismatch becomes sufficient to cause spontaneous microcracking within the composite during cooling from the sintering temperature⁴⁹.

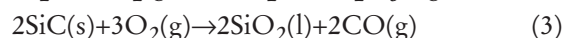
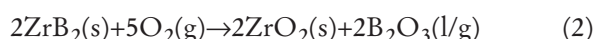
(3) Thermal properties and thermal shock resistance

For applications in hypersonic and re-entry systems, the thermal properties and thermal shock resistance of ZrB₂-SiC composites are of paramount importance. Thermal conductivity dictates how efficiently the material can dissipate heat from leading edges, thereby reducing thermal gradients and associated stresses. The thermal conductivity of monolithic ZrB₂ is relatively high for a ceramic (around 60 W/(m·K) at room temperature) and tends to increase with temperature⁴. The addition of SiC, which has a higher thermal conductivity (~120 W/(m·K)), generally increases the overall conductivity of the composite at room temperature⁵³. However, the temperature dependence is complex; studies have shown that while the conductivity of pure ZrB₂ increases with temperature, that of the ZrB₂-SiC composite can decrease, potentially due to increased phonon scattering at the numerous ZrB₂-SiC interfaces at higher temperatures⁵⁴.

Thermal shock resistance, the ability to withstand rapid temperature changes without catastrophic failure, is a critical performance metric. Theoretically, good thermal shock resistance is favored by a combination of high fracture strength (σ_f), high thermal conductivity (λ), low elastic modulus (E), and low coefficient of thermal expansion (α)⁵⁵. Based on their higher strength, ZrB₂-SiC composites are predicted to have superior thermal shock resistance compared to monolithic ZrB₂. However, experimental results often present a more complicated picture. Water quench tests, a common method for evaluating thermal shock, have in some cases revealed a similar critical temperature difference (ΔT_{crit}, the temperature drop that causes a significant strength reduction) of around 400 °C for both monolithic ZrB₂ and the composite. This discrepancy has been attributed to the large thermal expansion mismatch between the ZrB₂ matrix and SiC particles. During rapid quenching, this mismatch can lead to high localized interfacial stresses and non-uniform cooling, which can initiate microcracks and negate the benefit of the composite's higher bulk strength. The thermal shock behavior is further complicated by the testing environment. In an oxidizing atmosphere, surface oxidation can occur during heating, which may have a "crack-healing" effect by filling surface flaws with a viscous glass, thereby increasing the apparent thermal shock resistance⁵⁶. Conversely, repeated thermal shocks can lead to damage accumulation and degradation of the oxide scale, ultimately reducing the material's performance⁵⁷.

(4) Oxidation and ablation resistance

The primary motivation for adding SiC to ZrB₂ is to improve its performance in high-temperature oxidizing environments. The oxidation mechanism of ZrB₂-SiC composites is a complex, multi-step process that relies on the synergistic behavior of the two phases. At temperatures above 1 500 °C, both components oxidize according to the following reactions (2) and (3):



The oxidation of ZrB₂ produces a solid, refractory zirconia (ZrO₂) skeleton and liquid/gaseous boron oxide (B₂O₃). The oxidation of SiC produces liquid silica (SiO₂) and carbon monoxide gas. The key to the composite's protective capability is the reaction between the liquid B₂O₃ and SiO₂ to form a stable, viscous, low-vapor-pressure borosilicate glass. This glass phase permeates the porous ZrO₂ skeleton, sealing cracks and pores and forming a relatively dense surface layer that acts as an effective diffusion barrier, limiting the ingress of oxygen to the underlying unoxidized composite⁵⁸.

Despite this effective mechanism, a significant failure mode has been identified, particularly at very high temperatures (>1 800 °C) or under the high shear conditions of ablation. The formation of the protective silica-rich glass on the surface requires the consumption of SiC from the layer immediately beneath it. This process, combined with the outward diffusion of the glassy phase and the

evolution of gaseous species like CO and SiO, can lead to the formation of a porous and mechanically weak “SiC-depleted layer” between the outer oxide scale and the bulk composite⁵⁸. This depleted layer, consisting primarily of a porous ZrB₂ (or ZrO₂) network, is a critical structural flaw. It can act as a preferential site for crack initiation and can lead to the spallation or delamination of the entire protective oxide scale, catastrophically exposing the fresh composite surface to the oxidizing environment. A schematic of this multi-layer oxide structure is shown in Fig. 5.

The efficacy of the oxidation protection is strongly dependent on the microstructure created during processing^{59,60}. A fine and homogeneous distribution of SiC particles, as achieved through *in-situ* chemical synthesis, is essential for forming a continuous and uniform protective borosilicate glass layer. Composites with coarse or agglomerated SiC particles may fail to form a continuous glass seal, leaving regions of the ZrO₂ skeleton exposed and leading to localized, rapid oxidation and premature failure.

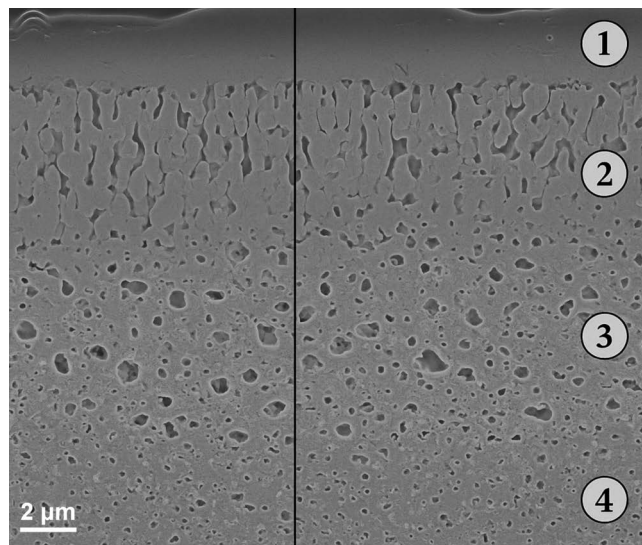


Fig. 5: Schematic cross-section illustrating the multi-layer oxide scale formation on a dense ZrB₂-SiC composite during high-temperature oxidation. .

Table 3: Influence of SiC content and microstructure on mechanical properties of sintered ZrB₂-SiC composites.

Composition (vol%)	Processing Route	ZrB ₂ Grain Size (μm)	SiC Particle Size (μm)	Flexural Strength (MPa)	Fracture Toughness (MPa·m ^{1/2})	Hardness (GPa)	References
ZrB ₂ (monolithic)	HP	~ 5.0	-	565 ± 53	3.6 ± 0.7	~ 22	61
ZrB ₂ – 30 % SiC	HP	-	4.4	1 150	-	21.4	49
ZrB ₂ – 30 % SiC	HP	-	> 11.5	< 500	-	< 20	49
ZrB ₂ - 30% SiC	HP	-	18.0	245	-	-	49
ZrB ₂ – 20 % SiC	Pressureless sinter	-	-	361 ± 44	4.0 ± 0.5	14.7 ± 0.2	44
ZrB ₂ – 20 % SiC	R-SPS	-	-	760 ± 19	6.3 ± 0.3	22.7 ± 1.4	46
ZrB ₂ – 30 % SiC	SPS	-	-	-	5.4	23.0	33
ZrB ₂ – 25 % SiC – 8 % Ni	SPS	-	-	-	8.3	-	33

Table 4: Oxidation behavior of ZrB₂-SiC composites at high temperatures.

Composition (vol%)	Test Conditions	Oxide Scale Thickness	Key Observations on Oxide Layer Structure	References
ZrB ₂ – 20 % SiC	1 500 °C, Air	~ 100 μm after 5 h	Formation of a protective borosilicate glass layer over a ZrO ₂ skeleton.	33
ZrB ₂ – 30 % SiC	1 650 °C, Air	Variable	Three-layer structure: SiO ₂ -rich top layer, ZrO ₂ rich middle layer, and a SiC-depleted inner layer.	33
ZrB ₂ – 10 % SiC	1 650 °C, Air	Variable	Single ZrO ₂ -rich oxide layer observed; less effective protection compared to higher SiC content.	33
ZrB ₂ -SiC-ZrC	> 2 000 °C, Rapid Heating	-	Addition of ZrC effectively reduced porosity in the SiC-depleted layer due to large volumetric expansion upon oxidation to ZrO ₂ .	62

Composition (vol%)	Test Conditions	Oxide Scale Thickness	Key Observations on Oxide Layer Structure	References
ZrB ₂ -SiC	> 1 800 °C, Air	-	SiC content significantly affects structure evolution; SiC-depleted layer formation depends on SiC distribution and environmental conditions.	63

V. Summary, Unresolved Challenges, and Future Outlook

This review has critically examined the intricate relationships between the *in-situ* synthesis of ZrB₂-SiC composite powders, their subsequent consolidation via various sintering techniques, and the resulting microstructures and properties of the final bulk ceramics. The state-of-the-art demonstrates a clear progression from conventional solid-state synthesis and hot pressing towards more sophisticated chemical and reactive processing routes. The central theme that emerges is the necessity of a holistic processing approach, where the synthesis of highly pure, fine-grained, and homogeneous powders is synergistically coupled with advanced, rapid sintering techniques that can preserve these desirable features in the final dense component. Chemical routes, particularly sol-gel and polymer-derived ceramic methods, offer unparalleled control over nanostructure and homogeneity, yielding powders with superior sintering activity. When paired with spark plasma sintering, these powders can be consolidated into fine-grained ceramics with enhanced mechanical properties. Reactive sintering further streamlines this pathway, representing a highly efficient method that combines synthesis and densification into a single step. The performance of these materials, particularly their resistance to thermal shock and oxidation, is directly governed by the microstructure – grain size, phase distribution, and purity – which is itself a direct consequence of this integrated processing chain.

Despite significant progress, several unresolved challenges and scientific controversies remain, which represent critical barriers to the widespread application of these materials. The most prominent challenge is the dichotomy between scalability/cost and microstructural control. While advanced chemical routes like PDC provide exquisite control over the final nanostructure, their complexity and reliance on expensive, air-sensitive precursors make them currently unsuitable for large-scale industrial production. A primary goal for future research is the development of scalable, cost-effective synthesis methods that do not compromise powder quality. Concurrently, the control of impurities, especially oxygen, remains a universal challenge. Oxygen contamination, whether from incomplete precursor reduction or atmospheric exposure, degrades both sinterability and high-temperature performance, and robust, oxygen-free processing chains are required. Even with *in-situ* methods, achieving perfect microstructural uniformity and eliminating defects like SiC agglomerates, which act as performance-limiting flaws, remains difficult. Finally, a complete mechanistic understanding of material behavior at the extreme temperatures of intended operation (> 2 000 °C) is still lacking. Controversies persist regarding the precise mechanisms of damage

versus healing during thermal shock and the exact kinetics governing the formation and degradation of the critical SiC-depleted layer during oxidation.

Looking forward, several promising research directions can be identified to address these challenges and advance the field. The development of novel, low-cost, high-yield single-source precursors for the PDC route is a high-priority area that could unlock the full potential of tailored nanocomposite architectures. The exploration of hybrid processing techniques, such as combining the energy efficiency of SHS with the moderating environment of a molten salt, or coupling field-assisted sintering with conventional pressure-assisted methods, may offer pathways to balance cost and performance. A crucial enabler for progress will be the increased application of advanced *in-situ* characterization techniques, such as high-temperature environmental transmission electron microscopy and synchrotron X-ray diffraction. These tools allow for the direct observation of phase evolution and microstructural changes during synthesis, sintering, and oxidation, providing invaluable data to validate and refine thermodynamic and kinetic models. This experimental work should be increasingly coupled with computational materials science. The use of CALPHAD (calculation of phase diagrams) modeling to predict phase equilibria in complex multi-component systems, and finite element analysis to simulate microstructural evolution and thermal stress distributions, will be indispensable for guiding experimental design, accelerating the discovery of new compositions, and optimizing processing pathways for the next generation of ultra-high temperature ceramics.

References

- Zoli, L., Servadei, F., Failla, S., Mor, M., Vinci, A., Galizia, P., Sciti, D.: ZrB₂-SiC ceramics toughened with oriented paper-derived graphite for a sustainable approach, *J. Adv. Cer.*, **13**, 207–219, (2024). doi: <https://doi.org/10.26599/JAC.2024.9220842>
- Lynam, A., Romero, A., Xu, F., Wellman, R., Hussain, T.: Thermal spraying of ultra-high temperature Ceramics: A review on processing routes and performance, *J. Therm. Spray Technol.*, **31**, 745–779, (2022). doi: <https://doi.org/10.1007/s11666-022-01381-5>
- Ni, D., Cheng, Y., Zhang, P., Liu, J., Zou, J., Chen, B., Wu, H., Li, H., Dong, S., Han, J., Zhang, X., Fu, Q., Zhang, G.: Advances in ultra-high temperature ceramics, composites, and coatings, *J. Adv. Ceram.*, **11**, 1–56, (2021). doi: <https://doi.org/10.1007/s40145-021-0550-6>
- Mihoob, M., Mohammed, H., Albarody, T., Ahmad, F., Alnarabiji, M.: Optimal process parameters for a thermal-sprayed molybdenum-reinforced zirconium diboride composite on a dummy substrate, *Energies*, **15**, 9415, (2022). doi: <https://doi.org/10.3390/en15249415>
- Choi, J., An, G.: The effects of the acid treatment of ZrB₂ particles on their purity and aqueous dispersibility, *Processes*, **10**, 18, (2021). doi: <https://doi.org/10.3390/pr10010018>

- 6 Venkatachalam, V., Esser, B., Binner, J.: Processing and performance of ultra high temperature ceramic matrix composite (UHTCMCs) using radio frequency assisted chemical vapour infiltration (RF-CVI), *Compos. Part A Appl. Sci.*, **185**, 108358, (2024). doi: <https://doi.org/10.1016/j.compositesa.2024.108358>
- 7 Quarto, M., Bissacco, G., D'Urso, G.: Study on ZrB₂-based ceramics reinforced with SiC fibers or whiskers machined by micro-electrical discharge machining, *Micromachines*, **11**, 959, (2020). doi: <https://doi.org/10.3390/mi11110959>
- 8 Cao, Y., Li, Y., Li, K., Deng, J., Zou, C., Hu, J., Chen, Z., Wen, J.: Synthesis and characterisation of sic-zrB₂ composite powders by Carbothermal/Borothermal reduction reaction, *Ceram. Silik.*, **68**, 598–609, (2024)
- 9 Lugovy, M., Orlovskaya, N., Neumann, M., Aneziris, C., Jelitto, H., Schneider, G., Kuebler, J.: Room temperature R-curve and stable crack growth behaviour of ZrB₂-SiC ceramic composites, *Adv. Appl. Ceram.*, **118**, 169–182, (2019). doi: <https://doi.org/10.1080/17436753.2018.1471443>
- 10 Jyoti, Tiwari, M., Singh, V.K.: Influence of SiC content to control morphology of *in-situ* synthesized ZrB₂-SiC composite through single-step reduction process, *Vacuum*, **203**, 111251, (2022). doi: <https://doi.org/10.1016/j.vacuum.2022.111251>
- 11 Khanra, A.K., Pathak, L.C., Mishra, S.K., Godkhindi, M.M.: Self-propagating-high-temperature synthesis (SHS) of ultrafine ZrB₂ powder, *J. Mater. Sci. Lett.*, **22**, 1189–1191, (2003). <https://doi.org/10.1023/A:1025336230885>
- 12 He, J., Gao, Y., Wang, Y., Fang, J., An, L.: Synthesis of ZrB₂-SiC nanocomposite powder via polymeric precursor route, *Ceram. Int.*, **43**, 1602–1607, (2017). doi: <https://doi.org/10.1016/j.ceramint.2016.10.073>
- 13 Riedel, R., Mera, G., Hauser, R., Klonczynski, A.: Silicon-based polymer-derived Ceramics: synthesis properties and Applications-A review, *J. Ceram. Soc. Jpn.*, **114**, 425–444, (2006). doi: <https://doi.org/10.2109/jcersj.114.425>
- 14 Bai, L., Ouyang, Y., Yuan, F.: Progress in preparation of ZrB₂ nanopowders based on traditional solid-state synthesis, *Nanomaterials*, **11**, 2345, (2021). doi: <https://doi.org/10.3390/nano11092345>
- 15 Zhao, B., Zhang, Y., Li, J., Yang, B., Wang, T., Hu, Y., Sun, D., Li, R., Yin, S., Feng, Z., Sato, T.: Morphology and mechanism study for the synthesis of ZrB₂ - SiC powders by different methods, *J. Solid State Chem.*, **207**, 1–5, (2013). doi: <https://doi.org/10.1016/j.jssc.2013.08.028>
- 16 Lian, X., Hua, X., Wang, X., Deng, L.: In situ growth behavior of SiC whiskers with high aspect ratio in the synthesis of ZrB₂-SiC composite powders, *Materials*, **13**, 3502, (2020). doi: <https://doi.org/10.3390/ma13163502>
- 17 Wu, W.W., Zhang, G.J., Kan, Y.M., Wang, P.L.: Reactive synthesis and mechanical properties of ZrB₂-SiC-ZrC composites, *Key Eng. Mater.*, **368**, 1758–1760, (2008). doi: <https://doi.org/10.4028/www.scientific.net/KEM.368-372.1758>
- 18 Xu, J., Ma, P., Zou, B., Yang, X.: Reaction behavior and formation mechanism of ZrB₂ and ZrC from the ni-zr-B₄C system during self-propagating high-temperature synthesis, *Materials*, **16**, 354, (2022). doi: <https://doi.org/10.3390/ma16010354>
- 19 Khanra, A.K., Pathak, L.C., Godkhindi, M.M.: Double SHS of ZrB₂ powder, *J. Mater. Process. Technol.*, **202**, 386–390, (2008). doi: <https://doi.org/10.1016/j.jmatprotec.2007.09.007>
- 20 Cao, Y., Zhang, H., Li, F., Lu, L., Zhang, S.: Preparation and characterization of ultrafine ZrB₂-SiC composite powders by a combined sol-gel and microwave boro/carbothermal reduction method, *Ceram. Int.*, **41**, 7823–7829, (2015). doi: <https://doi.org/10.1016/j.ceramint.2015.02.117>
- 21 Zhang, Y., Zhang, Y., Li, R.X., Yin, S., Sato, T., Li, J.P.: Synthesis of ZrB₂-SiC composite powders by sol-gel method using acetic acid as chemical modifier, *J. Taiwan Inst. Chem. Eng.*, **46**, 200–204, (2015). doi: <https://doi.org/10.1016/j.jtice.2014.09.022>
- 22 Yu, Z., Lv, X., Lai, S., Yang, L., Lei, W., Luan, X., Riedel, R.: ZrC-ZrB₂-SiC ceramic nanocomposites derived from a novel single-source precursor with high ceramic yield, *J. Adv. Ceram.*, **8**, 112–120, (2019). doi: <https://doi.org/10.1007/s40145-018-0299-8>
- 23 Polini, R., Marcucci, A., D'Ottavi, C., Nunziante, P., Filippis, P., Marcheselli, G.: Toward greener synthesis of WC powders for cemented tungsten carbides manufacturing, *ACS Sustain. Chem. Eng.*, **9**, 8458–8466, (2021). doi: <https://doi.org/10.1021/acssuschemeng.1c01286>
- 24 Ayodele, O., Babalola, B., Olubambi, P.: Evaluation of the wear and mechanical properties of titanium diboride-reinforced titanium matrix composites prepared by spark plasma sintering, *Materials*, **16**, 2078, (2023). doi: <https://doi.org/10.3390/ma16052078>
- 25 Hong, W., Gui, K., Hu, P., Zhang, X., Dong, S.: Preparation and characterization of high-performance ZrB₂-SiC-Cf composites sintered at 1450 °C, *J. Adv. Ceram.*, **6**, 110–119, (2017). doi: <https://doi.org/10.1007/s40145-017-02237>
- 26 Han, J.S., An, G.S., Choi, S.: Synthesis of ZrB₂@SiC composite particle through sol-gel and carbothermal reduction, *Mater. Today Commun.*, **33**, 104646, (2022). doi: <https://doi.org/10.1016/j.mtcomm.2022.104646>
- 27 Maître, A., Sallé, C., Boulesteix, R., Baumard, J., Rabinovitch, Y.: Effect of silica on the reactive sintering of polycrystalline Nd:YAG ceramics, *J. Am. Ceram. Soc.*, **91**, 406–413, (2008). doi: <https://doi.org/10.1111/j.1551-2916.2007.02168.x>
- 28 Azadi, A., O'Cearbhaill, E., Çelikin, M.: The effect of powder size and morphology on the sinterability of bioresorbable mg-sr/Ca alloys, *Miner. Met. Mater. Ser.*, 205–212, (2024). https://doi.org/10.1007/978-3-031-50240-8_39
- 29 Yao, H., Zhu, W., Zhu, X., Yi, X., Yao, J., Yuan, X., Chen, F., Han, X.: Development of Hydroxyapatite/Polycaprolactone composite biomaterials for laser powder bed Fusion: evaluation of powder characteristics, mechanical properties and biocompatibility, *Polymers*, **16**, 731, (2024). doi: <https://doi.org/10.3390/polym16060731>
- 30 Zhang, B., Xie, W., Lin, H., Wei, Z., Xiao, Z., He, K., Shi, Z.: Preparation of SiC coated graphite composite powders by nitriding combustion synthesis, *J. Adv. Ceram.*, **12**, 1930–1945, (2023). doi: <https://doi.org/10.26599/jac.2023.9220798>
- 31 Lange, F.: Sinterability of agglomerated powders, *J. Am. Ceram. Soc.*, **67**, 83–89, (1984). doi: <https://doi.org/10.1111/j.1151-2916.1984.tb09620.x>
- 32 Cheng, S., Yang, H., Nie, W., Wang, B., Wang, C., Dong, Y.: On the intrinsic sinterability of MgAl₂O₄ nanopowders, *J. Am. Ceram. Soc.*, **108**, e20577, (2025). doi: <https://doi.org/10.1111/jace.20577>
- 33 Patel, M., Reddy, J.J., Bhanu Prasad, V.V., Jayaram, V.: Strength of hot pressed ZrB₂-SiC composite after exposure to high temperatures (1000–1700 °C), *J. Eur. Ceram. Soc.*, **32**, 4455–4467, (2012). doi: <https://doi.org/10.1016/j.jeurceramsoc.2012.06.025>
- 34 Yao, W., Yan, J., Li, X., Chen, P., Zhu, Y., Zhu, B.: In situ ZrB₂ formation in B₄C ceramics and its strengthening mechanism on mechanical properties, *Materials*, **15**, 7961, (2022). doi: <https://doi.org/10.3390/ma15227961>
- 35 Savani, S., Alipour, M., Sharma, A., Karunakar, D.B.: Microwave sintering of ZrB₂-based ceramics: A review, *Synth. Sinter.*, **3**, 143–152, (2023). doi: <https://doi.org/10.53063/synsint.2023.33129>
- 36 Aguirre, T.G., Cramer, C.L., Cakmak, E., Lance, M.J., Lowden, R.A.: Processing and microstructure of ZrB₂-SiC

- composite prepared by reactive spark plasma sintering, *Results Mater.*, **11**, 100217, (2021).
doi: <https://doi.org/10.1016/j.rinma.2021.100217>
- 37 Yan, Y., Zhang, H., Huang, Z., Liu, J., Jiang, D.: In situ synthesis of ultrafine ZrB₂-SiC composite powders and the pressureless sintering behaviors, *J. Am. Ceram. Soc.*, **91**, 1372–1376, (2008).
doi: <https://doi.org/10.1111/j.1551-2916.2008.02296.x>
 - 38 Jiang, K., Liu, Y., Wang, J.-Y., Qi, Y.-S., Zhou, C.-L., Zhang, Q., Liu, R.-X., Tian, F., Yang, F.-H.: Preparation and properties of ZrB₂-SiC composite ceramics by pressureless sintering, *Adv. Ceram.*, **45**, 313–324, (2024).
doi: <https://doi.org/10.16253/j.cnki.37-1226/tq.2024.04.002>
 - 39 Akinribide, O., Mekgwe, G., Akinwamide, S., Gamaoun, F., Abeykoon, C., Johnson, O., Olubambi, P.: A review on optical properties and application of transparent ceramics, *J. Mater. Res. Technol.*, **21**, 712–738, (2022).
doi: <https://doi.org/10.1016/j.jmrt.2022.09.027>
 - 40 Haoxuan, G., Zhu, P., Lin, Q., Gao, M., De-ping, T., Zheng, X.: Sintering characteristics and microwave dielectric properties of BaTi₄O₉ ceramics with CuO-TiO₂ Addition, *Crystals*, **13**, 566, (2023).
doi: <https://doi.org/10.3390/cryst13040566>
 - 41 Sundari, R., Vijay, V., Shalini, V., Harish, S., Shimomura, M., Archana, J., Ponnusamy, S., Navaneethan, M.: Effective decoupling of grain boundaries and secondary phase interfaces for enhanced thermoelectric performance of Cu_{1.8}S/WS₂ nanocomposites, *J. Alloy. Compd.*, **960**, 170796, (2023).
doi: <https://doi.org/10.1016/j.jallcom.2023.170796>
 - 42 Švec, P., Čaplovič, L.: Microstructure and mechanical properties of b4c-tib2 composites reactive sintered from B₄C + TiO₂ precursors, *Process. Appl. Ceram.*, **16**, 358–366, (2022).
doi: <https://doi.org/10.2298/pac2204358s>
 - 43 Qin, M., Lou, Z., Zhang, P., Shi, Z., Xu, J., Chen, Y., Gao, F.: Enhancement of thermoelectric performance of Sr_{0.9}La_{0.1}TiO₃-based ceramics regulated by nanostructures, *ACS Appl. Mater. Interfaces*, **12**, 53899–53909, (2020).
doi: <https://doi.org/10.1021/acsami.0c13693>
 - 44 Zhang, H., Yan, Y., Huang, Z., Liu, X., Jiang, D.: Properties of ZrB₂-SiC ceramics by pressureless sintering, *J. Am. Ceram. Soc.*, **92**, 1599–1602, (2009).
doi: <https://doi.org/10.1111/j.1551-2916.2009.03039.x>
 - 45 Popov, O., Vleugels, J., Zeynalov, E., Vishnyakov, V.: Reactive hot pressing route for dense ZrB₂-SiC and ZrB₂-SiC-CNT ultra-high temperature ceramics, *J. Eur. Ceram. Soc.*, **40**, 5012–5019, (2020).
doi: <https://doi.org/10.1016/j.jeurceramsoc.2020.07.039>
 - 46 Sarkar, S., Kumar Mondal, M., Mallik, M.: Synthesis and characterization of ZrB₂-SiC composite powder, *Mater. Today Proc.*, **67**, 320–325, (2022).
doi: <https://doi.org/10.1016/j.matpr.2022.07.164>
 - 47 Li, C.-W., Lin, Y.-M., Wang, M.-F., Wang, C.-A.: Preparation and mechanical properties of ZrB₂-based ceramics using MoSi₂ as sintering aids, *Front. Mater. Sci. China*, **4**, 271–275, (2010).
doi: <https://doi.org/10.1007/s11706-010-0084-2>
 - 48 Fan, C., Liu, H., Zhou, J., Dai, X., He, H., Ye, Z.: Ultrastable and highly efficient CsPbBr₃ composites achieved by dual-matrix encapsulation for display devices, *InfoMat.*, **5**, e12417, (2023). doi: <https://doi.org/10.1002/inf2.12417>
 - 49 Watts, J., Hilmas, G., Fahrenholtz, W.G.: Mechanical characterization of ZrB₂-SiC composites with varying SiC particle sizes, *J. Am. Ceram. Soc.*, **94**, 4410–4418, (2011).
doi: <https://doi.org/10.1111/j.1551-2916.2011.04885.x>
 - 50 Pogozhev, Y., Potanin, A., Rupasov, S., Levashov, E., Volkova, V., Tashev, V., Timofeev, A.: Structure, properties and oxidation resistance of prospective HfB₂-SiC based ceramics, *Powder Metall. Funct. Coat.*, **41**–54, (2020).
doi: <https://doi.org/10.17073/1997-308x-2020-3-41-54>
 - 51 Sankarasabapathi, S., Subramaniam, N., Velmurugan, S., Nelson, G.: Exploring the mechanical and microstructural characterization of stir cast aluminum 8011 matrix hybrid composites, *Matéria*, **30**, e20240904, (2025).
doi: <https://doi.org/10.1590/1517-7076-rmat-2024-0904>
 - 52 Lai, L., Bi, Y., Niu, B., Yu, G., Li, Y., Ding, G., Xu, Q.: Reinforcement mechanisms and current research status of silicon carbide whisker-reinforced composites: A comprehensive review, *Rev. Adv. Mater. Sci.*, **63**, 20240047, (2024).
doi: <https://doi.org/10.1515/rams-2024-0047>
 - 53 Hu, C., Sakka, Y., Jang, B., Tanaka, H., Nishimura, T., Guo, S., Grasso, S.: Microstructure and properties of ZrB₂-SiC and HfB₂-SiC composites fabricated by spark plasma sintering (SPS) using TaSi₂ as sintering aid, *J. Ceram. Soc. Jpn.*, **118**, 997–1001, (2010). doi: <https://doi.org/10.2109/jcersj2.118.997>
 - 54 Zimmermann, J.W., Hilmas, G.E., Fahrenholtz, W.G., Dinwiddie, R.B., Porter, W.D., Wang, H.: Thermophysical properties of ZrB₂ and ZrB₂-SiC ceramics, *J. Am. Ceram. Soc.*, **91**, 1405–1411, (2008).
doi: <https://doi.org/10.1111/j.1551-2916.2008.02268.x>
 - 55 Zimmermann, J.W., Hilmas, G.E., Fahrenholtz, W.G.: Thermal shock resistance of ZrB₂ and ZrB₂-30% SiC, *Mater. Chem. Phys.*, **112**, 140–145, (2008).
doi: <https://doi.org/10.1016/j.matchemphys.2008.05.048>
 - 56 Yue, X., Peng, X., Wei, Z., Chen, X., Chen, X., Fu, T.: Repeated thermal shock behavior of ZrB₂-SiC-Graphite composite under pre-stress in air and ar atmospheres, *Materials*, **13**, 370, (2020).
doi: <https://doi.org/10.3390/ma13020370>
 - 57 Li, G., Chen, H.: Effect of repeated thermal shock on mechanical properties of ZrB₂-SiC-BN ceramic composites, *Sci. World J.*, **2014**, 419386, (2014).
doi: <https://doi.org/10.1155/2014/419386>
 - 58 Azari, K.K., Alizadeh, A., SayadiKelemi, A.: Investigating the research conducted on improving the properties of oxidation resistance and erosion of ZrB₂/SiC composites, *J. Environ. Friendly Mater.*, **7**, 51–63, (2023)
 - 59 Yu, L., Zhang, Y., Fu, T., Wang, J., Cui, K., Shen, F.: Rare earth elements enhanced the oxidation resistance of mo-si-based alloys for high temperature Application: A review, *Coatings*, **11**, 1144, (2021).
doi: <https://doi.org/10.3390/coatings11091144>
 - 60 Fattah-alhosseini, A., Molaei, M., Nouri, M., Babaei, K.: Review of the role of graphene and its derivatives in enhancing the performance of plasma electrolytic oxidation coatings on titanium and its alloys, *Appl. Surf. Sci. Adv.*, **6**, 100140, (2021).
doi: <https://doi.org/10.1016/j.apsadv.2021.100140>
 - 61 Grigoriev, O.N., Galanov, B.A., Kotenko, V.A., Ivanov, S.M., Koroteev, A.V., Brodnikovskiy, N.P.: Mechanical properties of ZrB₂-SiC(ZrSi₂) ceramics, *J. Eur. Ceram. Soc.*, **30**, 2173–2181, (2010).
doi: <https://doi.org/10.1016/j.jeurceramsoc.2010.03.022>
 - 62 Inoue, R., Arai, Y., Kubota, Y., Kogo, Y., Goto, K.: Oxidation of ZrB₂ and its composites: a review, *J. Mater. Sci.*, **53**, 14885–14906, (2018).
doi: <https://doi.org/10.1007/s10853-018-2601-0>
 - 63 Zhang, X.-H., Hu, P., Han, J.-C.: Structure evolution of ZrB₂-SiC during the oxidation in air, *J. Mater. Res.*, **23**, 1961–1972, (2008). doi: <https://doi.org/10.1557/JMR.2008.0251>