OXIDATION STUDIES ON SiC-TiB_2-ZrB_2 ULTRA HIGH TEMPERATURE MATERIAL USING SHOCK-TUBE

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Introduction:

The rapid advancement of hypersonic flight technology has created a pressing need for materials capable of withstanding the extreme thermal and oxidative environments encountered during atmospheric re-entry. When a spacecraft or ballistic missile re-enters the atmosphere at velocities exceeding Mach 5, the stagnation temperatures at leading edges and nose tips can exceed 2000°C, accompanied by intense convective and radiative heat flux. Conventional metallic and carbon-carbon composite thermal protection systems (TPS) face significant limitations in these regimes due to either excessive oxidation, ablation, or structural failure. This has driven sustained global research into Ultra High Temperature Ceramics (UHTCs), a class of transition metal borides, carbides, and nitrides that uniquely combine extreme melting points (>3000°C), high thermal conductivity, and intrinsic oxidation resistance.

Among UHTC candidates, Zirconium Diboride (ZrB_2) has emerged as one of the most extensively studied materials. ZrB_2 possesses a melting point of approximately 3245°C, high thermal conductivity (~60 W/m·K), good electrical conductivity, and moderate oxidation resistance. However, the oxidation of monolithic ZrB_2 produces a porous, low-viscosity ZrO_2 scale with an underlying B_2O_3 liquid layer that volatilises at temperatures above 1100°C, leaving a structurally deficient, non-protective oxide. This inadequacy at very high temperatures has motivated research into composite systems that exploit synergistic oxidation behaviour among multiple phases.

The incorporation of Silicon Carbide (SiC) as a secondary phase in ZrB_2 was a landmark development in UHTC research. During oxidation, SiC reacts with oxygen to form a SiO_2-rich glassy phase that dissolves B_2O_3 and fills surface pores, creating a dense, adherent borosilicate scale. This scale dramatically reduces oxygen diffusivity to the substrate and imparts self-healing capability against minor thermal cracking. Titanium Diboride (TiB_2), when added as a tertiary phase, contributes improved hardness (~25 GPa),

enhanced fracture toughness, and a higher-melting oxide layer (TiO_2, rutile), further stabilising the composite microstructure under extreme thermal loading.

The characterisation of UHTC oxidation behaviour under realistic conditions presents a significant experimental challenge. Standard isothermal furnace tests fail to replicate the transient, high-heating-rate flow conditions of an actual re-entry trajectory. The shock tube is a specialised aerodynamic facility that overcomes this limitation by generating shock waves that propagate through a test gas, creating short-duration high-temperature oxidising flow conditions with heating rates that closely represent flight environments. By mounting UHTC specimens directly in the test section, the shock tube subjects materials to aerothermal loads that are physically representative of flight, including rapid heating rates, high dynamic pressure, and reactive oxidising flows.

The present investigation, conducted at the Department of Aerospace Engineering, Global Academy of Technology, Bengaluru, under the KSCST 49th Series Student Project Programme, focuses on the systematic oxidation characterisation of SiC-TiB_2-ZrB_2 ternary UHTC composites using the shock tube facility. The study examines the influence of SiC volume fraction and TiB_2 addition on the nature, thickness, and protectiveness of the oxide scale formed under shock tube exposure at Mach numbers Ms = 1 to 2. Post-test specimens are characterised using Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (SEM-EDS) and X-Ray Diffraction (XRD) to elucidate oxide phase composition, scale morphology, and degradation mechanisms. The outcomes of this study provide valuable experimental data for the design and qualification of next-generation TPS materials.

Figure 1: Schematic diagram of the shock tube experimental setup used for high-enthalpy oxidation testing

Objectives:

1. To synthesise and characterise ZrB_2-SiC-TiB_2 UHTC composite specimens with varying SiC volume fractions (10 vol% and 20 vol%) using powder metallurgy and Spark Plasma Sintering (SPS), and establish their baseline microstructural and mechanical properties prior to oxidation testing.
2. To investigate the oxidation resistance of the fabricated SiC-TiB_2-ZrB_2 UHTC composites under simulated conditions using the shock tube facility at Mach numbers Ms = 1 to 2, and to document the resulting surface temperature exposure and oxide scale formation.

3. To evaluate and compare the oxidation performance of the composite system against monolithic ZrB_2 (baseline) through quantitative mass change measurements before and after shock tube exposure, thereby establishing oxidation kinetics and mass gain rates.
4. To analyse the effects of SiC addition on the formation, thickness, composition, and protectiveness of the oxide scale using Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) and X-Ray Diffraction (XRD) phase analysis.
5. To study the influence of TiB_2 incorporation on post-oxidation hardness retention, microstructural stability, and the suppression of spallation and micro-cracking in the oxide scale under thermal shock conditions.
6. To simulate transient thermal exposure using the shock tube setup at Mach 1–2, enabling controlled oxidative loading that cannot be adequately replicated through conventional furnace-based testing, and to correlate laboratory-scale shock tube results with expected TPS performance trends.
7. To develop a mechanistic understanding of the multi-layer oxide scale formation process (ZrO_2 outer layer, SiO_2-rich borosilicate interlayer) and identify the microstructural features and composition windows that maximise oxidation protection.

Methodology:

The experimental methodology is structured across three interconnected phases: composite fabrication, shock tube oxidation testing, and comprehensive post-test characterisation.

Phase 1 — Raw Material Procurement and Powder Characterisation: Commercial-grade ZrB_2 (purity ≥99%, average particle size 2–3 μm), SiC (≥98.5%, 1–2 μm), and TiB_2 (≥99%, 2–4 μm) powders are procured from certified suppliers. Prior to mixing, individual powders are characterised by XRD to confirm phase purity and by SEM to assess particle morphology. Particle size distribution is determined by laser diffraction analysis.

Phase 2 — Composite Powder Preparation and Mixing: Three composite compositions are prepared: (a) monolithic ZrB_2 (baseline), (b) ZrB_2–10 vol% SiC–10 vol% TiB_2, and (c) ZrB_2–20 vol% SiC–10 vol% TiB_2. Powders are weighed to ±0.01 g precision and subjected to high-energy ball milling at 250 rpm for 6 hours in anhydrous ethanol, followed by vacuum drying at 80°C for 12 hours. The resulting powder blends are sieved through a 150 μm mesh prior to consolidation.

Phase 3 — Specimen Consolidation by Spark Plasma Sintering (SPS): Densification is achieved using SPS at peak temperatures of 1850–1950°C (ramp rate: 100°C/min) under argon atmosphere with a 10-minute hold, yielding near-theoretical density (>97% TD) compacts. Final test coupons (20 mm × 20 mm × 3 mm) are machined using diamond-tipped cutting wheels and polished to a 1 μm finish.

Phase 4 — Pre-test Baseline Characterisation: Prior to shock tube exposure, specimens are characterised for bulk density (Archimedes method), Vickers hardness, fracture toughness (indentation method), initial surface morphology by SEM, and phase composition by XRD. Specimen mass is recorded to ±0.01 mg using a precision microbalance.

Phase 5 — Shock Tube Oxidation Experiments: The shock tube facility at Global Academy of Technology consists of a 50 mm internal-diameter driver section pressurised with helium and an air-filled driven section, separated by scored aluminium diaphragms. Shock Mach numbers Ms = 1 and Ms = 2 are achieved by controlling the driver-to-driven pressure ratio, producing post-shock static temperatures in the range 400–900°C respectively (calculated from Rankine-Hugoniot relations for air). Specimens are mounted flush with the driven section wall at the test station. Each test exposes the specimen to the high-temperature oxidising flow for a controlled duration of 2–10 ms. Surface temperature evolution is monitored using a two-colour pyrometer and embedded K-type thermocouples. Piezoelectric pressure transducers confirm Mach number and flow duration. A minimum of three repeat tests is conducted at each Mach number for each composition to ensure statistical reliability.

Phase 6 — Post-Exposure Characterisation: After shock tube testing, specimens are cross-sectioned, mounted in conductive epoxy, and polished to a 0.25 μm finish. FE-SEM imaging at 5–15 kV and EDS mapping are conducted to determine the spatial distribution of Zr, Si, Ti, B, O, and C across the oxide scale and substrate. XRD analysis of the post-test surface identifies all crystalline and amorphous oxide phases. Oxide scale thickness is measured from SEM cross-sections at a minimum of 10 locations per specimen. Mass change per unit exposed area (Δm/A, mg/cm²) is calculated from gravimetric data.

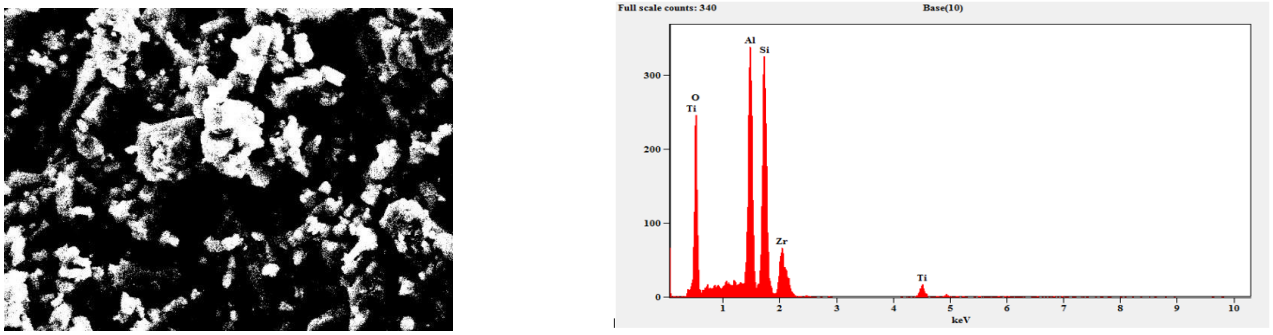


Figure 2: Representative SEM cross-section showing multilayer oxide scale on ZrB_2-20SiC-TiB_2 after shock tube exposure at Ms = 2

Result and Conclusion:

In conclusion, the SiC-TiB_2-ZrB_2 ternary UHTC composites demonstrate markedly superior oxidation resistance compared to monolithic ZrB_2 under all shock tube test conditions at Mach 1 to 2. The key findings are summarised below.

Oxide Scale Morphology (SEM-EDS):

Post-exposure SEM analysis of all composite specimens reveals the formation of a well-defined, adherent multilayer oxide scale. The outermost layer consists of a columnar-to-equiaxed ZrO_2 polycrystalline zone, immediately below which lies a dense, continuous SiO_2-rich borosilicate glassy phase. EDS mapping confirms silicon enrichment in the interlayer zone and zirconium dominance in the outer oxide. At the oxide-substrate interface, a thin depleted zone with reduced SiC content is observed, consistent with SiC consumption during scale formation. The oxide scales formed at Ms = 1 are thinner and more uniform compared to Ms = 2, where increased thermal loading produces a slightly more irregular outer ZrO_2

morphology. In contrast, the monolithic ZrB_2 baseline specimens exhibit a porous, cracked oxide scale with no continuous protective layer.

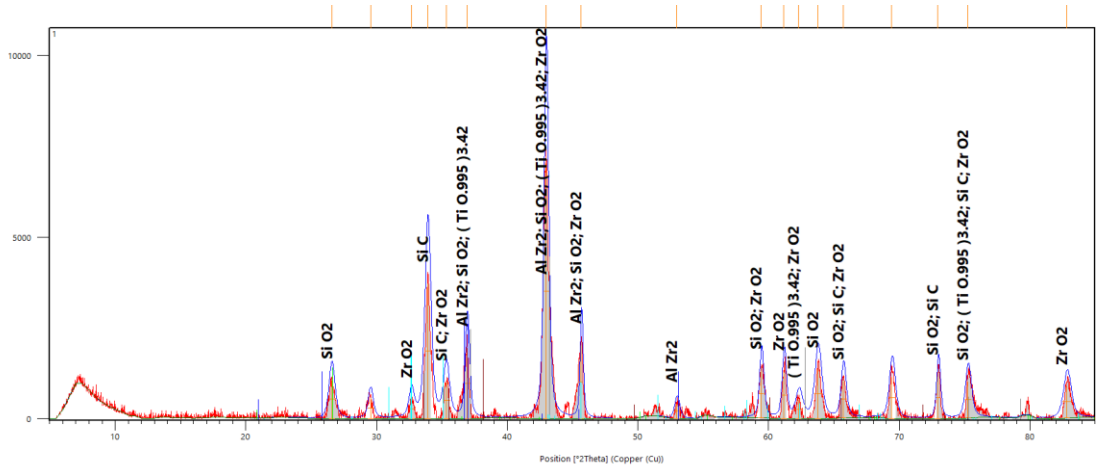
Phase Identification (XRD):

XRD analysis of post-test surfaces confirms the presence of monoclinic ZrO_2 (baddeleyite) as the primary crystalline oxide phase, with minor contributions from tetragonal ZrO_2. Broad amorphous humps in the 20–30° 2θ range confirm the presence of amorphous SiO_2 in the glassy interlayer. Rutile TiO_2 peaks are detected in all composite specimens, confirming active TiB_2 oxidation. No evidence of deleterious carbide or boride secondary phases is found in either the Ms = 1 or Ms = 2 exposed samples, indicating that the oxide scale remains chemically stable within the tested Mach range.

Oxidation Kinetics (Mass Gain):

Gravimetric analysis shows that composites exhibit significantly lower specific mass gain (Δm/A) than the monolithic baseline across both Mach numbers. The 20 vol% SiC composite consistently shows the lowest mass gain at both Ms = 1 and Ms = 2, confirming the beneficial role of higher SiC content in forming a more continuous and thicker borosilicate protective layer. The mass gain data follow parabolic kinetics, indicative of a diffusion-controlled, stable protective scale operating at both Mach conditions tested.

Mechanical Integrity Post-Oxidation: Post-test Vickers hardness measurements show that TiB_2 additions preserve substrate hardness more effectively than the SiC-only system. The ZrB_2–20SiC–10TiB_2 composition retains the highest percentage of its original hardness after both Ms = 1 and Ms = 2 exposures. No spallation is observed in any composite specimen at the Mach 1–2 range, confirming that the oxide scale remains mechanically adherent within this test envelope. These results validate ZrB_2-SiC-TiB_2 composites as viable TPS candidates and confirm that even at Mach 1–2 shock tube conditions, measurable and character sable oxidation behaviour is induced, providing a reliable entry-level dataset for the material system.



[Figure 3: Bar chart of mass gain vs. Mach number (Ms = 1, 2) for all compositions — insert graph]

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Future Scope:

The future scope of this project includes:

1. Composition Optimisation: Systematic investigation of higher SiC volume fractions (25–30 vol%) and variation in TiB_2 content (5–15 vol%) to identify the global optimum composition for maximum oxidation resistance. Incorporation of HfB_2 as a partial ZrB_2 substitute to exploit the higher-melting, more stable HfO_2 outer scale is also proposed.
2. Extension to Higher Mach Numbers: Extending the shock tube test matrix beyond Ms = 2 to cover Ms = 3–6, corresponding to surface temperatures of 1500°C and above, to characterise material behaviour under increasingly severe thermal environments and to bridge the gap between the current low-Mach dataset and hypersonic re-entry conditions.
3. Carbon Fibre-Reinforced UHTC Composites: Development of continuous carbon fibre-reinforced ZrB_2-SiC ceramic matrix composites (CMCs) to combine UHTC oxidation resistance with damage tolerance and thermal shock resistance provided by the fibrous architecture.
4. Thermal Cycling Studies: Investigation of the effect of repeated shock tube exposures on oxide scale fatigue, spallation propensity, and substrate depletion rates, critical for reusable TPS design.
5. Coupled CFD-Oxidation Numerical Modelling: Development of a computational model integrating hypersonic CFD flow solvers with a finite-element oxidation diffusion model, validated against the experimental shock tube data, to produce a predictive tool for TPS material behaviour across any re-entry trajectory.
6. Near-Net-Shape Component Fabrication and Arc-Jet Validation: Translation of optimised composite formulations from laboratory coupons to near-net-shape components using ceramic additive manufacturing, followed by arc-jet or plasma wind tunnel validation with ISRO and DRDO for eventual flight qualification.