

## PREFACE

Ultra-high temperature ceramics (UHTCs) are a prominent class of materials with high melting points (greater than 3000°C), excellent hardness, elastic modulus, and high thermal conductivity proposed for possible use as thermal protection systems and thermal shields in aerospace applications. The borides, carbides, and nitrides have been referred to as UHTCs. Among all borides, Zirconium diboride ( $ZrB_2$ ) is an impressive material of UHTCs having outstanding mechanical and chemical stability, e.g., low density, superior elastic modulus, high hardness, excellent strength, good chemical and thermal resistance. Along with these outstanding properties, some limitations have been observed, like low self-diffusion coefficient and covalent bond, which are responsible for poor sinterability. These limitations can be overcome by including sintering additives such as silicon carbide and zirconium carbide. Adding these additives to the  $ZrB_2$  ceramics can boost the densification, microstructure, and mechanical properties by restricting grain coarsening during synthesis and sintering. These additives provide the anti-oxidation behavior of the  $ZrB_2$  ceramics.

This thesis focuses on the synthesis, characterization, and mechanical properties of  $ZrB_2$ -based composites in the Zr-C-Si system with superior properties that can withstand ultra-high temperature conditions. The synthesis of a  $ZrB_2$ -based composite involves carefully selecting the starting composition and optimizing processing techniques. Low-cost zirconia and boron carbide are used for the synthesis of  $ZrB_2$ -based composite. Boron carbide is used as a reducing agent for zirconia. The solid-state reduction route synthesizes  $ZrB_2$ -based composite, followed by pressureless sintering/hot pressing methods. The optimization of the molar ratio or initial mole content within the Zr-C-Si system significantly impacts the ultimate composition of  $ZrB_2$ -based composites. The optimum amount of starting materials ensures that the resulting composite is perfectly tailored for ultra-high temperature applications. Characterizing the

synthesized ZrB<sub>2</sub> composites is crucial to understanding their structural and mechanical behavior under high-temperature conditions.

The results of this study expand our understanding of the synthesis, sintering, and characterization of ZrB<sub>2</sub>-based composites for thermal protection systems. A meticulous investigation examined the impact of in-situ formed additives, namely silicon carbide and zirconium carbide, on ZrB<sub>2</sub>-based composites. The study involved a comprehensive analysis of the resulting properties and performance of the composites incorporating these additives. The research employed various characterization techniques, including microstructural analysis, mechanical testing, and thermal properties evaluation. These additives hinder grain growth and provide fine microstructure during sintering. These additives also offer superior mechanical properties such as flexural strength, hardness and fracture toughness, and ablation resistance in extreme conditions.

The SiC and ZrC additives provide better dimensional and thermal stability during ablation at 2600°C due to the formation of SiO<sub>2</sub> and ZrO<sub>2</sub>/SiO<sub>2</sub> protective oxide layer on the surface of oxidized composites. Also, the SiO<sub>2</sub>-dense layer protects the base composite due to the low diffusion coefficient of oxygen and the development of the SiC-depleted layer. The findings provide valuable insights for designing and developing advanced ZrB<sub>2</sub>-based composites suitable for potential high-temperature applications.