Chapter: 1

Introduction

The present chapter gives a detailed overview of ceramics and composite materials. It also provides information about Ultra-High Temperature Ceramics (UHTCs), their synthesis, sintering, and mechanical properties. It includes the application of UHTCs in extreme conditions. Ceramics is a class of material composed of ionic, covalent, or mixed bonds. It has superior properties, including low density, exceptional thermal stability, corrosion resistance, and wear resistance. Thus, it has excellent potential for high-temperature, aerospace, and other structural applications. Traditional ceramics exhibit limitations in thermal shock resistance, oxidation resistance, and mechanical strength when subjected to ultra-high temperatures exceeding 2000°C.

In contrast, UHTCs stand out for their exceptional thermal and mechanical properties under extreme conditions. High-temperature ceramic components are used for load-bearing applications under medium to high temperatures (often exceeding 550°C), high stresses, and oxidizing/corrosive atmospheres. Within the realm of high-temperature ceramics, there is a distinct classification for ceramics characterized by a melting point exceeding 3000°C [1,2].

UHTCs are required to possess several key characteristics such as high melting point, excellent refractoriness, efficient thermal conductivity, low coefficient of thermal expansion (CTE), and exceptional resistance to various high-temperature phenomena such as oxidation, ablation, erosion, creep, and thermal shock (refer to Fig. 1.1). Recently, UHTCs have garnered attention for their potential use in aerospace applications, specifically in nose cones of hypersonic vehicles [3], leading edges of the wing, and rocket propulsion components[4].

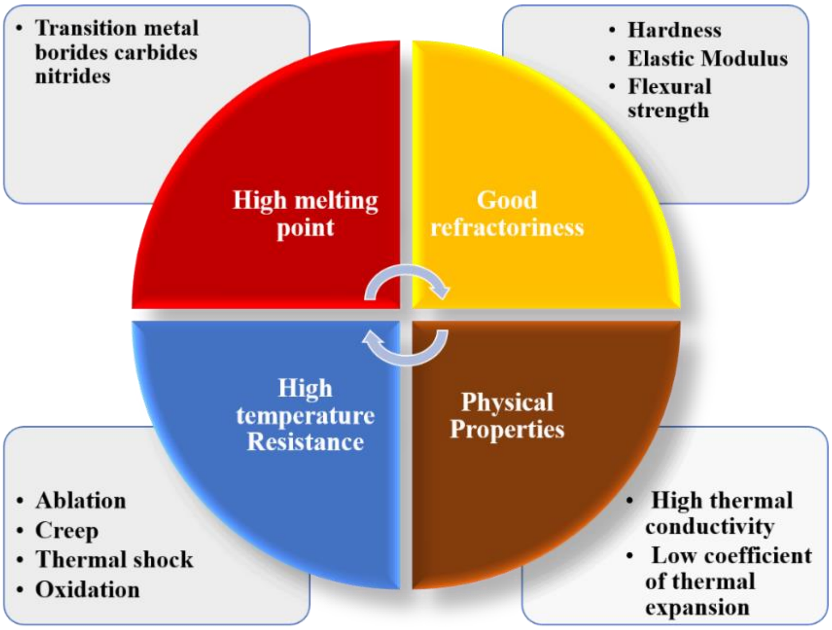

Fig. 1.1 Ultra-High Temperature Ceramics (UHTCs) key characteristics

UHTCs represent a group of refractory compounds, typically based on transition metal borides, carbides, and nitrides, that exhibit extraordinary resistance to degradation at temperatures beyond conventional ceramics. The classification of transition metal borides, carbides, and nitrides shown in Fig.1.2 helps illustrate the relationship and type of different transition metal compounds within the boride, carbide, and nitride families. Transition metal di-borides have undergone extensive research among the UHTCs, and their fundamental properties are mentioned in Table 1.1. These di-borides possess a unique combination of metal-like and ceramic-like characteristics. Specifically, they exhibit a range of densities from low to high (4.5–12.5 g/cc), with technologically relevant di-borides such as TiB_2 and ZrB_2 having densities toward the lower end of this spectrum. They also demonstrate a moderate coefficient of thermal expansion (CTE) ranging from 6.3 to 8.6 × 10^{-6} K^{-1}, high thermal conductivity (60–120 W/mK), low electrical resistivity (9–33 μΩ.cm), high elastic modulus (250–560 GPa), hardness (25–35 GPa), moderate fracture toughness (4–5 $MPam^{1/2}$), good flexural strength (300–1000 MPa), and oxidation resistance (at least up to 1200°C) (Refer to Table 1.1) [5–8].

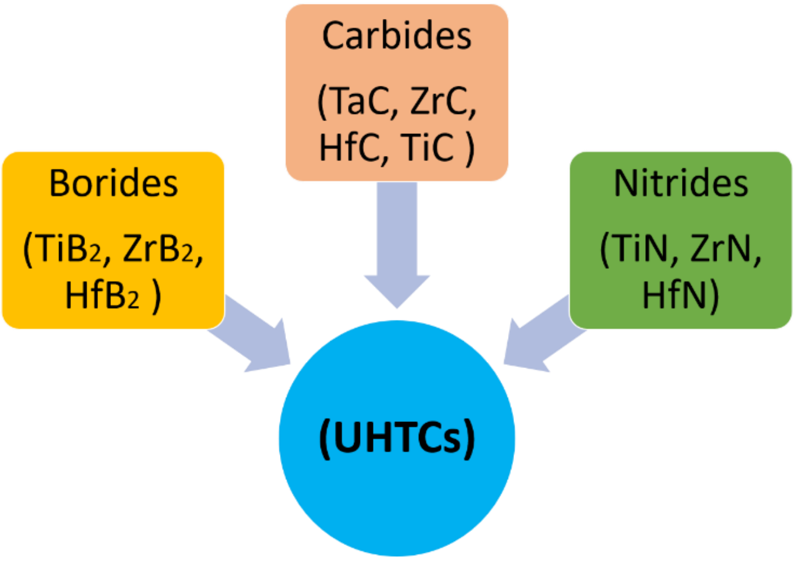

Fig. 1.2 Classification of different transition metal compounds within the boride, carbide, and nitride

Table 1.1 Fundamental physical, mechanical, and oxidation attributes of different ultra-high temperature ceramics

Material	Crystal structure	Melting point (°C)	Density (g/cc)	Thermal Conductivity (W m^{-1} K^{-1})	Electrical resistivity (μΩ.cm)	Elastic modulus(GPa)	Fracture Toughness (MPa.$m^{1/2}$)	Flexural Strength (MPa)
TiB2	HCP	3225	4.5	60-120	9-15	500-560	4-5	700-1000
ZrB_2	HCP	3200	6.1	60	10-32	340-500	4	300–400
HfB2	HCP	3380	11.2	104	11	480	4-5	300–450
TaB2	HCP	3040	12.5	-	33	248-551	4.5	555
HfC	FCC	3900	12.8	20	109	300-304		-
TaC	FCC	3800	14.5	-	-	470-540	3.4	600-700
ZrC	FCC	3530	6.6	20.5	63	480	2	400
TiC	FCC	3100	4.9	-	68	451	-	-
TiN	FCC	2950	5.4	19.2	-	-	-	-
ZrN	FCC	2950	7.3	20.5	-	380	-	330

These exceptional properties make transition metal di-borides suitable for a wide range of applications, including molten metal crucibles, cutting tools, wear-resistant parts, electrodes for electro-discharge machining, cathode material for electrical devices, armor materials, aluminum evaporation boats, neutron shields in nuclear applications, rocket nozzles, refractory parts, solar absorption applications, and high-temperature structural components, among others. Based on the di-borides life cycle as UHTCs, a reduction-oxidation reaction occurs where material flows from M (where M = Ti, Ta, Hf, Zr, etc.) to Processing, MB_2, Application, and MO_2. Within the broader family of UHTCs, this review primarily focuses on the di-borides of Ti, Ta, Hf, and Zr. Transition metal borides have excellent thermo-physical properties, and the oxidation resistance of di-borides makes them superior to other lightweight materials. Additionally, as good conductors of heat and electricity, di-borides are used not only as bulk structural parts but also as reinforcements or coatings to enhance the conductivity and other properties of polymers, ceramics, and metals. Due to their favorable electrical properties, di-borides can be designed into complex forms using electric discharge machining techniques [1,9].

Among all borides, Zirconium diboride (ZrB_2) stands out among transition metal borides due to its exceptional properties, making it suitable for aerospace and thermal power applications. It possesses the lowest theoretical density (6.1 g/cc), a low thermal expansion value ($6.8x10-6\ K^{-1}$), and a high melting point (3200°C). These attributes contribute to its desirability in various industries. ZrB_2 exhibits high hardness (20-25 GPa), high thermal conductivity ($60\ W\ m^{-1}\ K^{-1}$), moderate elastic modulus (340-500 GPa), and high flexural strength (300-400 MPa). Its hexagonal crystal structure with P6/mmm symmetry space group further enhances its properties. The bonding between zirconium (Zr) and boron (B) layers involves a strong covalent/ionic network structure. Zr-Zr metallic and B-B covalent bonds contribute to their elevated melting point, strength, and stiffness [10–12].

However, ZrB_2 ceramics have certain limitations due to challenges in sinterability, moderate fracture toughness, and difficulties in materials characterization at elevated temperatures. These issues collectively stimulate extensive research on this class of materials. Despite ongoing research efforts since the 1960s, these problems have yet to be fully resolved, and significant improvements are still needed for di-boride-based UHTCs.

Over the past two decades, research has focused on addressing processing-related problems associated with the requirement of high sintering temperatures, often necessitating the use of expensive processing equipment. Studies have explored the use of sintering additives (both metallic and ceramic sintering additives such as silicon carbide (SiC) [13–20], molybdenum disilicide ($MoSi_2$) [21–24], tungsten carbide (WC) [25–27], zirconium disilicide ($ZrSi_2$) [28], etc. novel sintering techniques (hot pressing and spark plasma sintering), and optimization of processing parameters. Another critical aspect of the research has been the improvement of fracture properties in UHTCs through microstructure and composition engineering, as well as the incorporation of various reinforcements. Similar strategies have been investigated to enhance thermal shock and oxidation resistance. Ensuring compatibility with the demanding application temperatures and stringent environmental conditions is crucial when tailoring the composition and microstructure.

Ultra-fine SiC can add to address the poor sinterability of single-phase ZrB_2. This addition reduces particle size and enhances the uniformity of the ZrB_2 composite. SiC exhibits favorable mechanical properties such as flexural strength (588.399 MPa), high hardness (23.53 GPa), moderate elastic modulus (421.68 GPa), and excellent thermal conductivity (146 W/mK) with a high melting point (2730°C). Additionally, SiC improves the oxidation resistance of ZrB_2 by forming a protective layer of borosilicate on its surface.

Binary or ternary-based systems have improved fracture toughness, oxidation resistance, and densification of ZrB_2 ceramics. One such additive is zirconium carbide (ZrC), a covalently bonded ceramic belonging to the transition metal group. ZrC ceramic possesses remarkable physical and chemical properties, making it valuable in refractory applications [29,30]. It exhibits a very high melting point (3420°C), high hardness (25.5 GPa), high modulus of elasticity (440 MPa), and high thermal conductivity (20 W/mK). Incorporating ZrC enhances oxidation resistance and inhibits grain coarsening in ZrB_2 [29–34].

Thesis outline

Designing suitable structural materials for ultra-high temperature applications requires consideration of parameters such as processing route optimization, composition, and microstructure improvement.

In Chapter 1, the introduction section of this article discusses the properties, limitations, and improvements (via the addition of compounds or other ceramics like ZrC & SiC) of UHTCs.

In Chapter 2, the subsequent sections delve into the literature review, including the crystal structure of UHTCs, processing routes for single-phase ZrB_2 and binary/ternary phase composites (ZrB_2–ZrC and ZrB_2–SiC), (ZrB_2–ZrC–SiC), optimization of sintering procedures, mechanical properties and oxidation resistance and ablation resistance at high temperature. This chapter also provides a detailed exploration of the research gap and the objectives of the present work to fulfill this gap. It offers a comprehensive overview of the specific goals and aims that drive the research study.

Chapter 3 of the research study develops into an in-depth exploration of the materials selection process and characterization techniques. This chapter explains the meticulous approach, methods, instruments, and procedures to thoroughly examine and analyze the chosen materials. The chapter elucidates the rationale behind the selection of each characterization technique, highlighting their strengths and relevance to the research goals.

Chapter 4 explains the influence of SiC content to control the in-situ synthesized ZrB_2-SiC composite morphology through the single-step reduction process.

Chapter 5 explains the comparative study of carbon and silicon sources for preparing the ZrB_2-SiC composite.

Chapter 6 explains the comparative study of microstructural and mechanical behavior of in-situ synthesized ZrB_2-ZrC and ZrB_2-SiC-ZrC composites.

Chapter 7 explains the effect of SiC on the ablation mechanism and morphological evolution of in situ synthesized ZrB_2-SiC composites.

Chapter 8 summarizes the findings of this research work and outlines specifics drawn from both the experimental and analytical efforts.