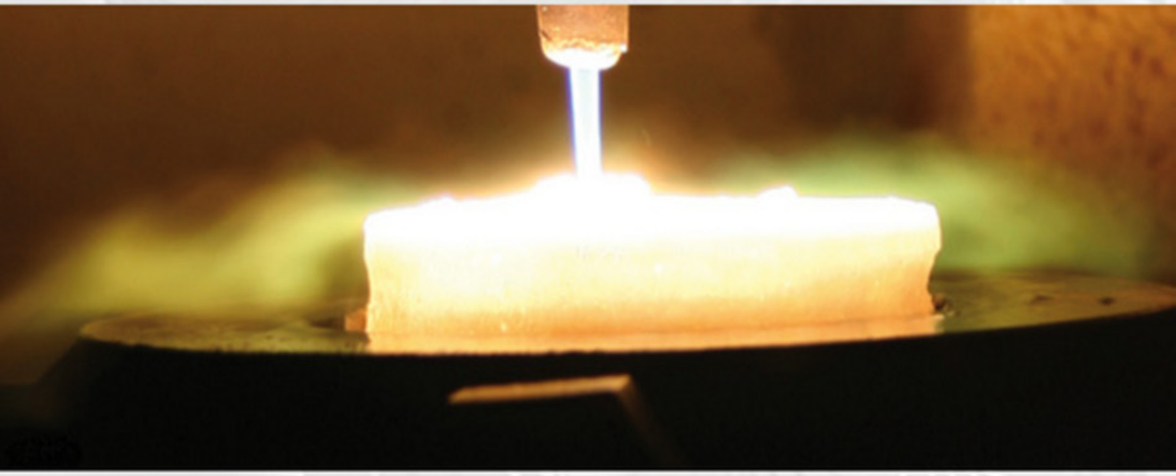
ULTRA-HIGH TEMPERATURE CERAMICS

MATERIALS FOR EXTREME ENVIRONMENT APPLICATIONS



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Cover Images: Title background shows crystal growth steps on the surface of a polycrystalline zirconium diboride ceramic (Courtesy of D. Sciti and F. Monteverde, Institute of Science and Technology for Ceramics); Main image shows a UHTC composite being tested in the flame of an oxyacetylene torch (Courtesy of J. Binner, University of Birmingham).

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The editors would like to dedicate this book to the memory of Dr. Jules Routbort who provided the impetus and support for the first UHTC meeting. Unfortunately, Jules passed away in early 2012 before the meeting was held.

CONTENTS

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1

INTRODUCTION

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1.1 BACKGROUND

The impetus for this book was the conference "Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications II," which was held on May 13–18, 2012, in Hernstein, Austria. As the title implies, this was the second conference on this topic that has been organized by Engineering Conferences International (ECI). The four editors served as the co-organizers of the conference. Both the U.S. Navy Office of Naval Research Global and the U.S. Air Force European Office of Aerospace Research and Development provided funding for the conference that helped support participation of invited speakers and students. The conference brought together about 60 researchers from around the world to discuss the latest research related to this remarkable class of materials. The first conference in the series was organized by Eric Wuchina and Alida

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Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications, First Edition.
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Bellosi and was held in August 2008 at Lake Tahoe, California, United States. A third conference is planned for Australia in April 2015.

The book is our attempt to capture a snapshot of the current state of the art in ultra-high temperature ceramic (UHTC) materials. The chapters in this volume represent the key areas that were discussed in the meeting. The chapter authors are leaders in their fields from around the world, and all of the lead authors participated in the conference. Rather than a narrow focus on the latest scientific progress as would be expected in an article in a peer-reviewed journal, the chapters in this book provide a broader look at recent progress and information on the current understanding of this family of materials.

1.2 ULTRA-HIGH TEMPERATURE CERAMICS

Recent interest in UHTCs has been motivated by the search for materials that can withstand extreme environments. The extremes can include, individually or in combination, the effects of temperature, chemical reactivity, mechanical stress, radiation, and wear. Some potential applications for this class of materials include microelectronics, molten metal containment, high-temperature electrodes, and wear-resistant surfaces. However, a majority of the research has been motivated by unmet material needs for hypersonic aviation. Specifically, improved materials are needed to withstand the conditions encountered by wing leading edges and propulsion system components in hypersonic aerospace vehicles as well as the extreme conditions associated with atmospheric reentry and rocket propulsion. The combination of extreme temperature, chemically aggressive environments, and rapid heating/cooling is beyond the capabilities of current engineering ceramics. Recent interest in UHTCs has been high as indicated by a number of special journal issues [1–3] and review articles [4–9] devoted to the topic. Despite this interest, no clear criteria have been established to differentiate UHTCs from other structural ceramics.

Broadly, ceramic materials can be defined as inorganic, nonmetallic solids [10]. This definition encompasses most materials that are typically considered to be ceramics such as clay-based traditional ceramics, alumina, piezoelectric materials, and silicon carbide. However, the definition still leaves some gray areas such as glass, carbon, and intermetallic compounds. In some cases, the definition is expanded to include other characteristics. For example, Barsoum defines ceramics as “solid compounds that are formed by the application of heat, and sometimes heat and pressure, comprising at least one metal and a non-metallic elemental solid, a combination of at least two nonmetallic elemental solids, or a combination of at least two nonmetallic elemental solids and a nonmetal” [11]. In other cases, the definition involves characteristics such as melting temperature, bonding type, or electrical properties [12]. Likewise, several different definitions have been espoused for UHTCs. The three main classifications are melting temperature, ultimate use temperature, and chemical composition.

The most common definition for a UHTC is a material that melts at a temperature of 3000°C or higher. As shown in Figure 1.1, very few materials meet this criterion. For example, only three elements have melting temperature above 3000°C, W, Re, and Ta, all of which are metals. Note that carbon was not included in this group because of the complexity of its behavior, which has been reviewed in detail elsewhere [13, 14]. Interestingly, ThO_2 is the only oxide ceramic that has a melting temperature above

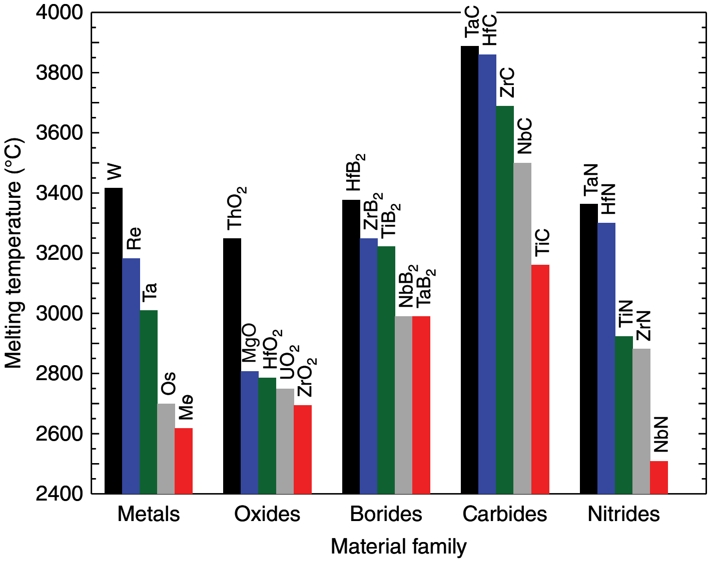

Figure 1.1. Materials with the highest reported melting temperature grouped by material family. Reprinted with permission from Ref. [6].

3000°C. Most of the materials that have melting temperatures above 3000°C are borides, carbides, and nitrides of early transition metals. Consequently, most studies on UHTCs focus on compounds such as ZrB_2, HfB_2, TaC, TaB_2, ZrC, and HfC. While this definition is probably the most common, significant uncertainty exists in melting temperatures for these compounds. For example, ZrB_2 is commonly reported to melt at 3250°C based on the phase diagrams reported by Rudy [15] and Portnoi *et al.* [16], but others report different melting temperatures including 3040°C by Glaser and Post [17] and 3517°C by Rogl and Potter [18] The discrepancies indicate that not only are temperatures difficult to measure precisely in the ultra-high temperature regime, but also that these compounds may decompose or dissociate before melting, which would also be difficult to detect in the experimental setups used for these studies. So, while melting temperature is a clearly defined metric, assessment includes uncertainty. Further, the selection of 3000°C as the criterion was arbitrary and could be set at other temperatures.

A second method that can be used to define UHTCs is the highest temperature for use in air. This practical definition fits well with the nature of engineering materials, but introduces additional questions. As with melting temperature, the selection of a use temperature to define the ultra-high temperature regime is also somewhat arbitrary. At the time of publication of this chapter, a number of choices are available for use in air at temperatures up to about 1600 °C including alumina, magnesia, silicon carbide, and silicon nitride. Hence, the minimum use temperature for the ultra-high temperature regime should be above that level. Many hypersonic applications involve higher temperatures, so 2000 °C has been cited as the cutoff of the ultra-high temperature regime [5–19]. Despite a seemingly clear definition, both use temperature and duration blur the distinction. The application-driven criterion to define UHTCs has obvious attractions as a definition for engineering materials, but this metric also has some shortcomings.

The final method that can be used to define UHTCs is chemistry, which is the least quantitative, but probably most widely used. Most UHTC compounds are borides, carbides, or nitrides of early transition metals. Hence, any compound containing a transition metal such as Zr, Hf, Ta, W, or Nb along with B, C, or N has the potential to be a UHTC.

No one definition has emerged as the way to identify UHTCs. As an example of the shortcomings of all of the three definitions described earlier, consider one of the most commonly cited UHTC compositions, ZrB_2–SiC. When compounds with melting temperatures above 3000 °C such as ZrB_2 are combined intentionally with other phases (i.e., sintering aids, grain pinning additives, oxidation-enhancing additives, etc.) or when impurities are present, the temperature at which liquid forms or melting occurs can be below 3000°C. For ZrB_2–SiC, the solidus temperature is about 2300°C due to a eutectic reaction [20]. Hence, one could argue that one of the most widely researched UHTC compositions does not meet any of the criteria defined earlier because: (i) liquid forms below 3000°C; (ii) one of the constituents (SiC) cannot be used for extended times above 1600°C; and (iii) SiC is not a boride, carbide, or nitride of an early transition metal.

Despite the uncertainty in the definition of UHTCs, a close-knit global community of researchers who focus on these materials has emerged over the past decade or so. Groups in the United States, Italy, China, Australia, Russia, and the United Kingdom, have worked competitively and collaboratively to advance our understanding of the fundamental behavior of materials that can be used in extreme environments. This book, in keeping with the spirit of the ECI conference series, takes a pragmatic approach in defining UHTCs and includes the community of researchers who focus on materials with the potential for use in extreme environments such as those associated with hypersonic flight, atmospheric reentry, and rocket propulsion. Since the first conference in the series in 2008, the community of researchers has grown to include those working on materials for nuclear applications and researchers who are investigating new methods for characterizing and testing materials under conditions that are representative of the extreme environments encountered in use.

1.3 DESCRIPTION OF CONTENTS

The sequence of the chapters in this book was selected to represent the progression of a typical experimental study. After this introductory chapter, the next chapter provides background information on previous research. The chapter focuses on historic studies on what we now consider UHTCs that were conducted in the United States in the 1950s, 1960s, and 1970s. These studies accompanied decisions that were being made about the design of the next generation of launch and reentry vehicles. The next group of chapters describes synthesis and processing. The third chapter describes synthesis of boride compounds, while the fourth focuses on calculations of fundamental bonding properties. The fifth chapter describes aqueous processing and surface chemistry. The sixth is the final chapter in the synthesis and processing section, and it describes densification and microstructure of UHTCs. The middle section of the book contains chapters describing the properties of UHTCs. This section includes contributions focused on thermomechanical properties, elevated temperature mechanical properties and deformation, and oxidation. The final section is focused on the performance of UHTC materials. The section includes a review of UHTC-based composites. Other chapters focus on TaC, UHTC nitrides, TiB_2, and UHTCs for nuclear applications. The final chapter describes the testing of UHTCs in relevant environments. That chapter is based on the conference keynote presentation.

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2

A HISTORICAL PERSPECTIVE ON RESEARCH RELATED TO ULTRA-HIGH TEMPERATURE CERAMICS*

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2.1 ULTRA-HIGH TEMPERATURE CERAMICS

Historically, the boride and carbide ceramics that we now classify as ultra-high temperature ceramics (UHTCs) have been known by a number of different names including refractory borides or carbides [1–4], oxidation-resistant diborides [5], ceramals or cermets [6, 7], and hard metals [8]. Although the term **ultra-high temperature** was not used in any of these early reports, the aerospace community recognized the need for materials that could withstand the extreme temperatures and chemically aggressive environments. For example, reports from the late 1950s and early 1960s from the National Advisory Committee for Aeronautics (NACA) and its follow-on agency the National Aeronautics and Space Administration (NASA) described the need for rocket nozzles and thermal protection systems [2, 6, 9, 10]. In particular, Reference [10] identified heat sources associated with atmospheric reentry and rocket propulsion as well as

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*This manuscript references a number of technical reports from projects sponsored or conducted by the U.S. Government. All of these reports have been approved for public release and are available either through the NASA Technical Report Server (http://ntrs.nasa.gov/search.jsp) or the Defense Technical Information Center (http://www.dtic.mil/dtic/).

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TABLE 2.1. Selected recommendations for future research and development activities related to UHTCs from Reference [10]

Recommendation number	Recommendation
10	A systematic investigation on the application of TPS to solid propellant rocket motors to include (i) transpiration, (ii) evaporation cooling, (iii) chemical reaction cooling, (iv) heat sink, (v) radiation, (vi) film cooling, and (vii) ablation.
12	Studies on the materials behavior at extreme temperatures, and establishment of **thermal and other pertinent material properties at extremely high** as well as extremely low temperatures.
13	Development and introduction of standard test methods for the establishment of performance data for TPS.
16	Reduction of efforts in short-time high-heating-rate ablative systems for ballistic nose cones, as all present and foreseen requirements can be adequately met with achieved capabilities. Remaining efforts should be directed toward a wider variety of potential material systems.
18	Reduction of present extensive efforts of theoretical treatment of TPS in favor of technological approaches as outlined in (12) above

the needs related to leading edges, acreage, and propulsion components. The report provided a series of recommendations for future studies, and some of the pertinent recommendations are summarized in Table 2.1. Interestingly, some of the needs identified more than 50 years ago continue to be cited as priorities for current research. The Streurer report also defined heat flux and time regimes in which different types of thermal protection systems would be most effective [10]. As shown in Figure 2.1, convection and radiation cooling could be used for long-duration exposures at heat fluxes below about 40 BTU/ft^2·s (~45 W/cm^2), whereas a heat sink approach could be used for short-duration (i.e., <0.3 min) exposures for heat fluxes up to about 1000 BTU/ft^2·s (1130 W/cm^2). Either ablative materials or transpiration cooling was recommended for heat fluxes above 1000 BTU/ft^2·s (1130 W/cm^2).

Although the term UHTCs is a recent development, the term **extreme** associated with the application environments began to appear in the ceramic refractories literature in the late 1950s. Extreme was used to refer to temperatures of 2500°F (~1400°C) or higher [11, 12]. The broader term **ultra-high temperature** emerged in the 1960s and found more widespread use in Japanese articles through the 1990s [13–16]. Terms similar to **ultra-high temperature ceramics** started to appear in a series of reports and papers when the current wave of interest in these materials started in the United States in the late 1980s and early 1990s [17–21]. Reference [20] is notable as it clearly defined the ultra-high temperature regime in terms of temperature (above 3000°F or ~1650°C) as well as providing a minimum strength target (greater than ~150 MPa) for materials at ultra-high temperatures (Fig. 2.2). The NASA report [21] seems to have been particularly influential in solidifying the use of the term

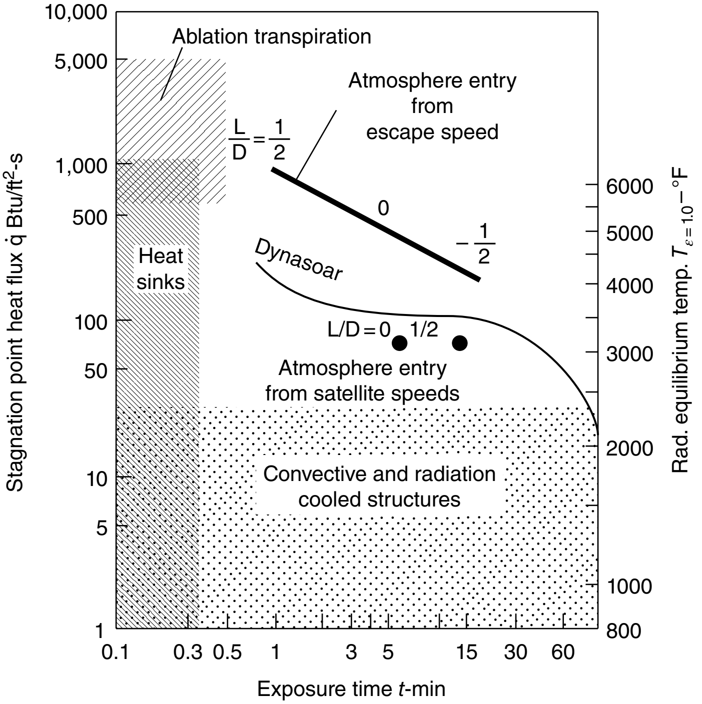

Figure 2.1. Summary of types of thermal protection systems as a function of heat flux and exposure time from Reference [10].

UHTC as it clearly identified this class of materials as candidates for hypersonic aerospace vehicles. The subsequent Sharp Hypersonic Aerothermodynamic Research Probe (SHARP) tests drew significant attention to UHTCs. In particular, the SHARP B-1 and B-2 tests as well as the related NASA reports identified UHTCs as potential candidates for the hypersonic flight environment despite failure of the UHTC strakes due to problems traced back to processing issues [22, 23]. The term UHTC and the recent resurgence of interest in research on boride and carbide UHTCs seem to have grown from these studies as well as those from a select group of other researchers [24–26].

2.2 HISTORIC RESEARCH

The synthesis of boride and carbide compounds began to draw the interest of researchers in the late 1800s and early 1900s. For the diborides, Tucker and Moody reacted elemental zirconium and boron to produce ZrB_2, although they described the compound as Zr_3B_4 [27, 28]. McKenna later reported the synthesis of ZrB_2 by carbothermal reduction according to Reaction 1 at 2000°C [29]. In contrast, reports

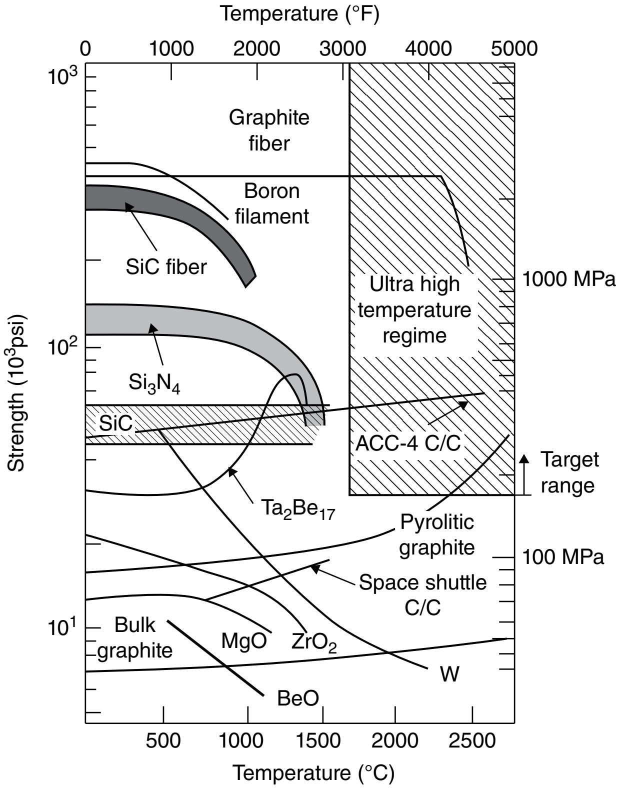

Figure 2.2. Strength as a function of temperature for several engineering materials along with a clearly defined Ultra-High temperature regime from Reference [20].

of the formation of HfB_2 were much later, presumably due to the difficulty of separating Hf from Zr [30].

$$ZrO_{2(cr)} + B_2O_{3(l)} + 5C_{(s)} \rightarrow ZrB_{2(cr)} + 5CO_{(g)} \qquad (2.1)$$

Henri Moissan was an early pioneer of research on carbide materials with over 600 scientific publications identified in a literature search.† Even though Acheson was the first to report a commercially viable synthesis process for SiC [31], Moissan's research on SiC [32], as well as the carbides of Mo [33], Ti [34], and Zr [35] was notable because of its breadth and depth. After the initial reports, scientific publications on borides and many of the carbides were sporadic, but progress was made in areas such as bonding [36], electrical properties [37], and electronic structure [38] through the first half of the 1900s. Although limited in scope, these early studies set the stage for the progress that would result from later studies.

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†SciFinder Scholar, accessed June 6, 2012.

2.3 INITIAL NASA STUDIES

In the late 1950s and early 1960s, NASA (and its predecessor agency NACA) began to search for materials that could be used in the extreme environments associated with rocket propulsion and atmospheric reentry. The agency was exploring supersonic flight with vehicles such as the Bell X-1, which was the first plane to fly faster than the speed of sound, as well as a variety of concepts for hypersonic aerospace vehicles [39]. NASA conceived, studied, and tested both blunt body and lifting body designs [40]. Even in the early 1950s, NASA recognized that current materials technologies were not adequate to enable their future vehicle needs and began to search for suitable candidates [6]. For rocket motors, extreme temperatures were predicted for some applications, so the list of candidates of interest was limited to materials with melting points above 6000°F (~3300°C) including tungsten, pyrolytic graphite, hafnium carbide, and tantalum carbide [2]. In contrast, a wider variety of materials were needed for the thermal protection systems of future manned and unmanned vehicles. The agency recognized that their array of planned vehicles would present a wide variety of thermal loads based on the trajectories and other needs of specific missions [10]. For example, significant differences in heat loads were identified based on whether vehicles would land vertically as was planned for the Mercury program or horizontally as was foreseen for winged vehicles (Fig. 2.3) [41]. Because of the possible trajectories that were being considered (Fig. 2.4) and the different possible wing leading-edge radii [41], a variety of materials were considered candidates including refractory metals, ceramics, and cermets [42]. At this point, heat loads

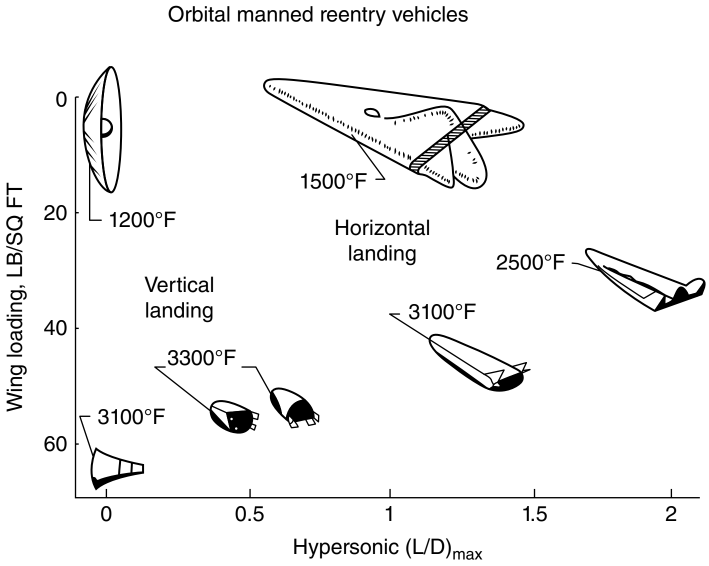

Figure 2.3. Notional temperature requirements for orbital reentry vehicles based on projected wing loading and hypersonic lift-to-drag (L/D) ratio from Reference [41].

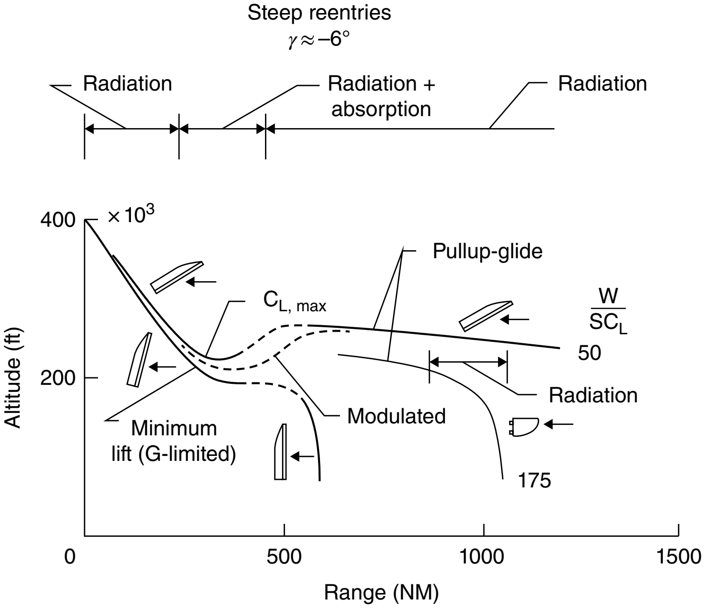

Figure 2.4. Trajectories and methods for dealing with heat loads from Reference [41].

could be predicted, and the fundamental design principles used to develop thermal protection systems for specific trajectories had been established, but neither standardized evaluation tests nor design databases populated with candidate materials were available [10]. Availability of standardized tests and design data is a problem that persist for sharp leading-edge vehicles to the present day. These early studies also motivated the U.S. Air Force to explore vehicle designs with higher cross range, which motivated interest in transition metal boride compounds. Ultimately, the blunt body Space Shuttle Orbiter was selected as the first reusable atmospheric reentry vehicle based on cost and mission flexibility [39]. However, the early studies showed the potential advantages of hypersonic vehicles with a high lift to drag ratio such as substantially higher cross range.

2.4 RESEARCH FUNDED BY THE AIR FORCE MATERIALS LABORATORY

Beginning in the early 1960s, the U.S. Air Force funded a series of studies that focused on refractory diborides and carbides as candidates for a number of potential future aerospace vehicles. For this manuscript, the research has been divided into three main categories: (1) initial thermodynamic analysis and oxidation behavior; (2) processing, properties, oxidation, and testing studies; and (3) phase equilibria research. Each of these areas is discussed in the following subsections.

2.4.1 Thermodynamic Analysis and Oxidation Behavior

Through the first half of the 1960s, the U.S. Air Force commissioned studies focused on the thermodynamic properties of refractory compounds, including the borides, carbides, and nitrides. Broad-based studies at AVCO produced fundamental thermodynamic property data for an extensive number of borides, carbides, and nitrides [43]. Data generated as part of that project continue to be cited today in references such as the NIST-JANAF tables [44]. Building on the AVCO studies, investigations at Arthur D. Little, Inc. focused on the preparation and characterization, thermodynamic data, and reaction kinetics of ZrB_2 and HfB_2 [45]. These investigations had a number of notable outcomes. The materials studied in this project were produced using zone melting techniques to remove impurities and minimize porosity. As shown in Figure 2.5, both ZrB_2 and HfB_2 exhibited parabolic oxidation kinetics over wide temperature ranges, with HfB_2 having

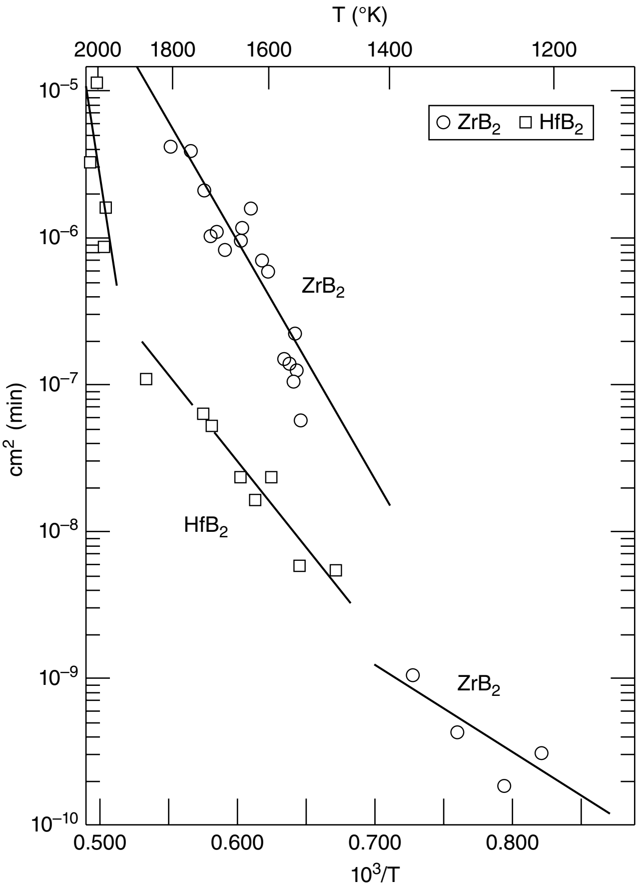

Figure 2.5. Comparison of kinetic rate constants for the oxidation of ZrB_2 and HfB_2 as a function of temperature [45].

lower overall rate constants based on lower mass gain. This research resulted in a number of scientific publications describing the oxidation of nominally pure diborides that continue to be referenced today [46, 47] This research also provided fundamental thermodynamic data including heat capacity values for ZrB_2 and HfB_2, which were more accurate than previous reports because of the higher purity of the materials examined in this study. In addition, Arthur D. Little performed early research on the oxidation of silicide compounds [48].

The U.S. Air Force also sponsored several projects that examined the thermodynamic aspects of refractory compounds. Research at the National Bureau of Standards (NBS; now the National Institute of Standards and Technology of NIST) examined the heats of formation of ZrB_2, AlB_2, and TiB_2 [49]. The NBS report is notable because of an extensive literature review of the synthesis of the borides of Al, Ce, Cr, La, Mg, La, Mo, Nb, P, Si, Sr, Ta, Th, Ti, W, U, and V. Other research examined the oxidation of carbides [50] and the vaporization of refractory compounds including ZrO_2, HfO_2, ThO_2, ZrB_2, and HfN [51]. More than 50 years later, the fundamental research sponsored by the U.S. Air Force continues to serve as the basis for understanding the thermochemical stability of borides and carbides.

2.4.2 Processing, Properties, Oxidation, and Testing

ManLabs, Inc., a small research and development company located in Cambridge, Massachusetts, was the lead contractor on a series of projects focused on boride and carbide ceramics. These projects started in the early 1960s and continued into the 1970s. A number of notable accomplishments were achieved, which resulted in the publication of a large number of highly detailed technical reports as well as a series of publications in scientific journals. While the focus was on using commercially available materials, the team provided feedback to suppliers such as improving the purity or reducing the particle size of the starting powders. In addition, several specialized pieces of equipment were produced for processing, characterizing, and testing these materials due to the extreme temperatures involved. The projects were divided into three different focus areas. In the first series, candidate materials were screened along with the evaluation of processing and characterization methods. The second series focused on measuring and understanding the properties of ZrB_2 and HfB_2 ceramics. The final series of reports focused on the evaluation of boride-, carbide-, and graphite-based materials in relevant environments. This subsection attempts to capture some of the research highlights from each series of reports in roughly the time sequence of the projects.

The first series of studies at ManLabs examined TiB_2, ZrB_2, HfB_2, NbB_2, and TaB_2 as potential candidates for hypersonic flight and atmospheric reentry applications [52]. Based on literature reports of melting temperatures and thermochemical stability, borides were identified as promising candidates. This first study focused on gathering chemical, physical, and thermodynamic property data for candidate materials from literature sources and then identifying the most promising materials for further study with some initial oxidation testing. Based on oxidation rates, HfB_2 and ZrB_2 were selected for further study. The follow-on study examined the effect of boron-to-metal ratio (B/Me) on oxidation behavior, thermal conductivity, emissivity, and electrical resistivity [53].

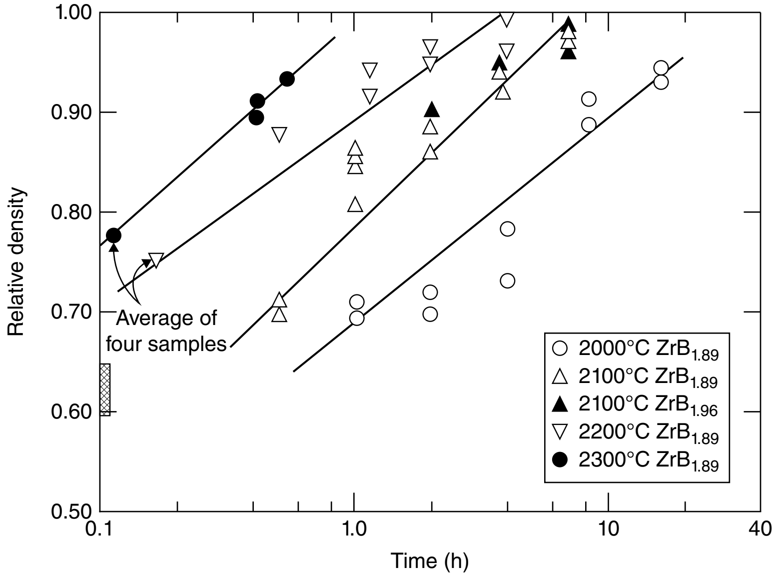

Figure 2.6. Relative density as a function of sintering time for ZrB_2 with different B/Me ratios [53].

This study also reported extensive evaluations of the densification behavior of ZrB_2 and HfB_2. While stoichiometric ZrB_2 and HfB_2 could not be hot pressed to relative densities of more than 98% with grain sizes of less than 50 μm, altering the B/Me ratio improved densification. As shown in Figure 2.6, ZrB_2 with a B/Me ratio of 1.89 could be hot pressed to nearly full density at 2200°C without exaggerated grain growth. The plot also shows that hot pressing at 2300°C resulted in a limiting density value of less than 95%, which was attributed to entrapped porosity. Further analysis of density as a function of grain size and sintering time (Fig. 2.7) was used to elucidate the densification mechanism. Densification was attributed to grain boundary diffusion through a thin liquid film where impurities were concentrated. This study also examined the oxidation behavior of the nominally pure diborides as well as diborides with additions of Si or $MoSi_2$. While detailed kinetic studies were completed as part of a project described later, this project did define regimes of behavior for protective behavior (i.e., below ~1200°C for nominally pure ZrB_2) and linear kinetics that are still in use today. The report ended with sections describing the thermodynamic stability and phase equilibria of the diborides that were based on literature reports and thermodynamic calculations. The most important outcome of the first two studies was that it motivated additional projects that were more focused on fundamental research on the processing, microstructure, properties, and performance of boride ceramics.

In the second series of studies, borides with carbon and silicon carbide additions were examined. As part of this project, a series of ZrB_2 and HfB_2 compositions were formulated and densified. The addition of SiC was examined to improve the oxidation resistance of the diborides while carbon was added to improve thermal shock resistance.