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Ultra-high temperature ceramics: Materials for extreme environments

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ABSTRACT

This paper identifies gaps in the present state of knowledge and describes emerging research directions for ultra-high temperature ceramics. Borides, carbides, and nitrides of early transition metals such as Zr, Hf, Nb, and Ta have the highest melting points of any known compounds, making them suitable for use in extreme environments. Studies of synthesis, processing, densification, thermal properties, mechanical behavior, and oxidation of ultra-high temperature ceramics have generated a substantial base of knowledge, but left unanswered questions. Emerging research directions include testing/characterization in extreme environments, composites, computational studies, and new materials.

1. Introduction

Ultra-high temperature ceramics (UHTCs) are an emerging class of materials that have the potential for use in extreme environments [1,2]. Most often, UHTCs are defined as compounds that have melting points above 3000 °C (Fig. 1) [3]. Several alternative definitions have been proposed with the most pragmatic being that UHTCs are ceramic materials that can be used for extended times at temperatures above 1650 °C [4]. However, none of these definitions captures the wide range of extreme conditions in which UHTCs may be used. Chemically, nearly all UHTCs are binary compounds in which boron, carbon, or nitrogen combine with one of the early transition metals (TMs) such as Zr, Hf, Ti, Nb, and Ta [5]. The strong covalent bonds between the TMs and B, C, or N result in compounds with high hardness, stiffness, and melting temperature [6]. These compounds also exhibit higher electrical and thermal conductivities than oxide ceramics due to varying degrees of metallic bond character. This intriguing combination of metal-like and ceramic-like properties allow UHTCs to survive extreme temperatures, heat fluxes, radiation levels, mechanical loads, chemical reactivities, and other conditions that are beyond the capabilities of existing structural materials.

Reports of the synthesis of UHTCs date back to the late 1800s [7,8], but technological interest in these materials grew dramatically during the space race that started in the late 1950s and extended through the 1960s. At that time, groups in the Soviet Union and the U.S. were searching for materials to be used in rocket motors, heat shields, and structural components for the first generation of spacecraft [9,10]. These vehicles were going to encounter heat fluxes and temperatures for durations that were beyond the capabilities of traditional approaches such as transpiration cooling, heat sinks, and convective/radiative cooling [11]. The technological challenges motivated a tremendous body of research conducted by scientists including G.V. Samsonov, H. Nowotny, E.V. Clougherty, and L. Kaufman. Publications produced by these researchers and their collaborators document fundamental understanding of the bonding, electronic structure, thermodynamic properties, mechanical behavior, phase equilibria, and oxidation response of UHTCs. After this initial surge of interest, research on these materials waned for several decades.

Interest in UHTCs was renewed in the late 1980s, again due to aerospace applications such as scramjet propulsion, hypersonic aerospace vehicles, and advanced rocket motors [4,12–15]. For example, in the U.S., the National Aeronautics and Space Administration (NASA) and the U.S. Air Force built and flew vehicles as a means to test technologies needed for sustained hypersonic flight (Fig. 2). One of the technological challenges was presented by the designs, which included sharp leading edges and control surfaces. At hypersonic speeds, the bow shock at these sharp features produces temperatures in excess of 2000 °C, heat fluxes of hundreds of Watts per square cm, and highly reactive dissociated gas species [16]. Diboride-based UHTCs were considered for these applications based on the combination of thermal conductivity, strength at elevated temperature, and oxidation resistance [17], while carbides and nitrides have received more attention for components such as nozzle throats, divert/attitude control thrusters, and nozzle liners where higher thermal and mechanical loads are encountered [18].

In this paper, continuing challenges in areas of recent research activity are identified followed by an assessment of emerging trends and an outlook for future research.

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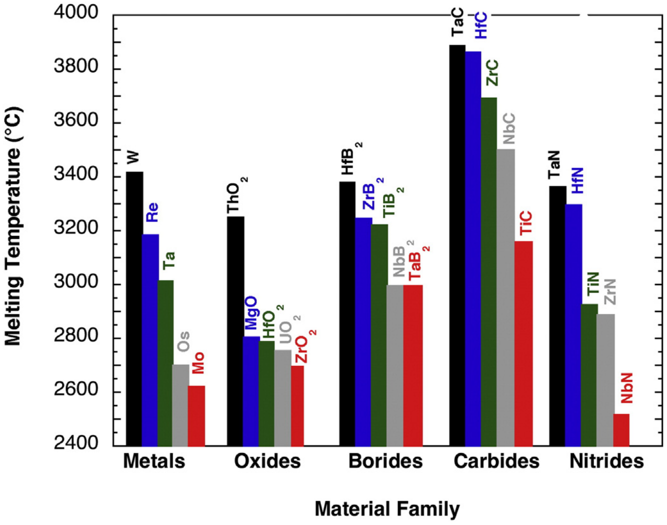

Fig. 1. Melting temperature for elements and compounds from different families of materials showing that very few materials have melting temperatures above 3000 °C. Reprinted by permission from Fahrenholtz et al. [3].

2. Continuing challenges

Research on UHTCs during the past 25 years has furthered the state of knowledge in several important areas including synthesis, processing, densification, thermomechanical properties, and oxidation. Despite these advances, key gaps in the understanding of UHTCs remain. Research groups in the U.S., China, Japan, the U.K., Italy, India, and other countries have on-going efforts focused in these areas.

Most commercial UHTCs are synthesized by carbothermal reduction of the corresponding oxide [19,20]. Limitations of this method include the relatively coarse particle sizes and substantial levels (i.e., 0.1 wt% or higher) of impurities including other metals, oxygen, nitrogen, and/or carbon. Despite these limitations, a majority of the recent studies of UHTCs have utilized commercial powders. Alternative synthesis methods can produce powders with finer particle sizes, higher purities, or controlled shapes [21]. Processes based on solid-state reactions have been the most popular routes, but processes utilizing liquid or polymer precursors have been pursued to enable deposition of coatings or polymer infiltration and pyrolysis (PIP) processing of UHTC-matrix composites. Most of the liquid/polymer processes reported to date have involved two steps whereby the precursors decompose to an oxide with or without carbon/boron, which is then reacted to form the desired UHTC phase (Fig. 3) [22]. Some recent advances have surmounted this obstacle by directly synthesizing borides or carbides in a single step [23]. Continuing research challenges in synthesis include synthesizing higher purity UHTC powders, identifying mechanisms and kinetics of synthesis reactions, and designing liquid/polymer precursors that have higher ceramic yields and are less sensitive to degradation under ambient conditions.

Fig. 2. Photograph of the X-51 flight vehicle mounted on the wing of a B-52 prior to a test flight. The X-51 holds the record for the longest duration hypersonic flight by an aircraft. Note the heads of engineers on the lower left of the image for scale. Image is public domain from NASA.

Most often, UHTCs are processed as dry powders using conventional forming methods such as dry pressing. A limited number of studies have reported novel aspects of dispersion [24], colloidal forming [25], and plastic forming methods [26,27], revealing fundamental aspects of the surface chemistry of UHTCs while also enabling near-net shape forming. Processing and synthesis have substantial synergy whereby improvements in synthesis that control the size, shape, or surface chemistry of UHTC powders impact the ability to form stable dispersions and develop desired rheological properties in suspensions, pastes, or plastic masses. Very few studies have addressed the fundamental processing science of UHTCs resulting in opportunities to explore control of powder surface chemistry, produce slurries and pastes with high solids loadings, develop additive manufacturing processes, and devise aqueous processing routes that do not increase the oxygen impurity content of the resulting ceramics.

Sintering of non-oxide ceramics, and particularly UHTCs, involves a competition between densifying and coarsening mechanisms [28]. The presence of oxygen and other impurities promotes coarsening mechanisms that produce porosity trapped within grains, exaggerated grain growth, or other phenomena, which prevent ceramics from reaching full relative density (Fig. 4) [29]. Finer starting particle sizes can enhance sintering, but oxygen contents must be below certain critical levels for full densification. While pressure-assisted methods such as hot pressing, hot isostatic pressing, and spark plasma sintering are the most common methods for densification, pressureless sintering can be accomplished in some systems through the use of additives [30–32]. Despite practical knowledge for densification, only a few publications have reported detailed information on the fundamental transport mechanisms for densification or the kinetics of sintering processes leaving ample room for additional basic research in these areas.

A multitude of studies have described the room temperature thermal and mechanical properties of UHTCs with the most important properties being strength, hardness, elastic constants, thermal conductivity, and fracture toughness. Most of these studies have reported properties for a single ceramic without identifying fundamental factors related to composition, microstructure, porosity, impurities, etc. that control observed behavior. Presentation of properties without understanding of structure-property relations presents a particular challenge for UHTCs. A single report of poor properties or sub-standard performance in a ground test can turn potential users against an entire class of materials, even if the material in question failed due to extrinsic factors that could have been addressed had the root cause of failure been studied. Systematic studies have elucidated microstructure-mechanical property relationships and identified strength-limiting flaws to the extent that ceramics with desired properties can be designed by controlling grain size for nominally pure, fully dense ZrB_2 or SiC cluster size in ZrB_2-SiC ceramics. Studies have also begun to address the fundamental factors that are responsible for the wide variety of room temperature thermal conductivities reported for ZrB_2-based ceramics (Fig. 5) and other UHTCs [33–36]. Additional research is needed to isolate fundamental factors that control thermal and mechanical behavior for compositions other than ZrB_2 or ZrB_2-SiC, examine elevated temperature structure-property relationships, and report intrinsic properties of UHTCs.

Oxidation behavior, or, more broadly, resistance to aggressive chemical environments, is critical in the extreme environments that might be encountered by UHTCs include oxidation above 1600 °C, reaction

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