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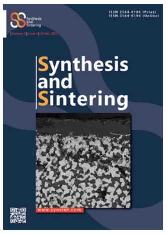

Review article

Recent advances in synthesis of ultra-high temperature ceramic matrix composites

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ABSTRACT

A ceramic material designed for ultra-high temperatures (UHTCs) generally comprised of nitrides, carbides, and borides derived from transition metal elements, with a particular focus on compounds belonging to TaC and Group IVB (Hf and Zr). Hypersonic vehicle nozzles and engine components can take advantage of the unique characteristics of these materials. A broad range of coatings and composites based on UHTC is currently being developed to conquer the inherent fragility, weak thermal shock resistance, and brittleness of bulk ceramics. Ultra-high temperature materials with high entropy have gained considerable attention in recent years. A review of the current state of the art of UHTC composites and coatings will be provided in this report. Properties and processing approaches to achieve the microstructure will be discussed further.

KEYWORDS

Advanced ceramics
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Infiltration

1. Introduction

The use of ultra-high temperature ceramics (UHTCs) in severe conditions has recently become more prevalent [1]. A UHTC is typically defined as a compound with a melting temperature above 3000 °C [2]. UHTCs are ceramics that show good stability at temperatures greater than 1650 °C. Many definitions of UHTCs have been stated that describe their stability in harsh environments, however, these definitions are short or do not describe these ceramics well [3]. A UHTC is a binary compound consisting of boron, carbon, or nitrogen and an early transition metal (TM), such as Hf, Zr, Nb, Ti, or Ta. TMs can form strong covalent bonds with C, B, or N to yield parts with high stiffness, hardness, and melting temperatures. Because of changing degrees of metallic bond features, these compounds are also more electrically and thermally conductive than oxide ceramics. The UHTCs, which have the properties of both metal and ceramic, can be employed in a broad range of conditions, such as extreme temperatures, high radiation levels, rapid heat fluxes, mechanical loads, chemical reactivity, and others that would normally be impossible for structural materials to endure [4, 5]. Despite the fact that UHTC materials have been synthesized since the late 1800s, the industrial concern in UHTC materials has grown rapidly since the late 1950s, when the space race began, and which continued into the 1960s. As part of the first generation of spacecraft, both the United States and the Soviet Union tried to find materials for heat shields, rocket motors, and structural components [1, 6]. Compared to traditional approaches with heat sinks, transpiration cooling, and radiative/convective cooling, such vehicles were likely to encounter temperatures and heat fluxes for longer periods. Nowotny, Samsonov, Kaufman, and Clougherty have conducted tremendous research to respond to technological challenges. As the aerospace sector gained a lot of interest in UHTC technology in the late 1980s, UHTC engineering became a hot topic due to applications like hypersonic vehicles, scramjet propulsion, and modern rocket motors [1]. It has already been established that high entropy alloys (HEA) have advanced the compositional space of metallurgy by exhibiting impressive thermomechanical properties, such as wear resistance, high strength, and oxidation resistance at ambient and high temperatures [7]. To maximize configurational entropy

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(ΔS_{mix}=R.lnN, N: number of equimolar components, R: gas constant) HEA normally comprises 4 or 5 elements mixed in equimolar concentrations. Gibbs free energy (G=H-TS, H: enthalpy, T: temperature, S: entropy) minimization determines thermodynamic stability at constant pressure. At high temperatures, -TS term (known as HE phases) may become dominant, leading to the possibility that HE phases could be more stable [8, 9]. In multi-component solid solutions, this entropic term stabilizes the solution into a single phase. Following recent studies, it has been proven that IVB transition metal diborides, because of their unique features such as resistance to oxidation and erosion, high thermal conductivity, mechanical properties, and high chemical stability, facilitate the achievement of ultra-high temperature ceramic materials [10]. HfB_2 and ZrB_2 are two of the most studied candidates [10–13]. Such materials are highly covalently bonded, leading to high melting temperatures, high strength, and chemical resistance. Furthermore, MB_2's low self-diffusion coefficient and high percentage of covalent bonds make it difficult to densify [3]. However, MB_2, due to defects such as unstable mechanical properties, low fracture toughness, and subcritical crack growth, limits its use in industrial applications [14]. Disadvantages such as low thermal shock and oxidation resistance and the unreliability of mechanical properties at high temperatures are some of the obstacles that prevent their wide usage in ultra-high temperature conditions. The addition of sintering aids and high pressures are two methods to increase the sinterability of diboride materials, which are used to improve the properties of MB_2 ceramics [15].

2. Carbon fibers-reinforced ultra-high temperature ceramics

Heat-resistant materials are used to ensure the structural integrity of hypersonic vehicles during re-entry or hypersonic cruise [16]. Composites of carbon fiber-reinforced carbon matrix (C/C) show potential heat resistance due to their low density. A C/C composite can withstand temperatures as high as 2500 °C in an inert environment [17]. Because of oxidation and CO and CO_2 generation in an oxidizing atmosphere at 400 °C, such materials dramatically suffer from consumption of material. As a result, the C/C composite cannot be used in extreme environments [18]. To increase C/C composite oxidation and recession resistance, coatings including Al_2O_3, SiC, Ir, ZrO_2, and SiO_2 are used. A SiO_2 scale forms on the C/C composite surface coated with SiC, giving them excellent resistance against oxidation up to 1800 °C [19, 20]. The delamination of coating, however, causes intensive oxidation of C/C composites, which is why coatings cannot provide an effective solution for improved oxidation resistance. Composites reinforced with carbon fibers can also be made using SiC as a matrix. SiC-based composites were fabricated with continuous carbon fiber reinforcement. Composites made from this material exhibit resistance to oxidation up to 1800 °C, similar to those made from C/C composites coated with SiC [21]. Even if partial delamination or damage to the silica layer is induced on the surface of C/SiC under an oxidizing atmosphere, a continuous silica layer is created on the surface. Oxygen partial pressure in the system strongly influences the SiC oxidation performance. The formation of gaseous SiO occurs when oxygen partially permeates the system, as well as SiC reacts with oxygen (active oxidation) [21, 22]. Over 1800 °C, C/SiC composites undergo drastic recession due to the absence of the SiO_2 layer. At extremely elevated temperatures, C/SiC composites are limited by their oxidation behavior. A UHTC matrix has been used as a matrix for C_f-reinforced ceramic matrix composites (CMCs) to enhance the ablation resistance under oxidizing atmosphere [23]. Because of their melting points of > 2500 °C, Hf-based (HfC, HfB_2, and HfN) and Zr-based (ZrC, ZrB_2, and ZrN), UHTCs can be considered as potential CMC matrix materials. The surface of some UHTCs forms an oxide layer. As a result of such oxide layers covering the surface, they are oxidation resistant at conditions as hot as 2000 °C even when exposed to oxygen [23, 24].

3. Fabrication process

3.1. Hot-pressing (HP)

Structured ceramics and composites are typically fabricated by hot-pressing (HP). Fabricating monolithic UHTCs with HP is challenging due to their low self-diffusion constants and high melting points (~2000 °C) [25]. A 98–99% relative density has been achieved with UHTC compacts sintered by HP, pressureless sintering (PS), and spark plasma sintering (SPS) [26]. Despite the fact that continuous carbon fiber-reinforced UHTCs can be made using the same procedure as monolithic ones, fabricating such complex structures can be challenging [27]. Recent study by Vicni et al. [23] has demonstrated the manufacturing of C_f-strengthened ZrB_2 ceramics (C_f/ZrB_2) through HP. Combining the slurry infiltration and sintering process produced a weak fiber/matrix interface in these studies. Fiber/matrix interfaces were strengthened by the sintering process. Because B_2O_3 and ZrO_2 impurities in UHTC starting powders react with carbon fibers in the following way [28, 29]:

$$2B_2O_3(l) + 7C(s) \rightarrow B_4C(s) + 6CO(g) \quad (1)$$

$$ZrO_2(s) + 3C(s) \rightarrow ZrC(s) + 2CO(g) \quad (2)$$

Fibers are often bonded to matrix proteins and fail as a result of bridging, delamination, or cracking without hardening mechanisms [30].

3.2. Chemical vapor infiltration (CVI)

Graphite pores were reduced and nuclear fuel particles were bonded with the CVI process in the 1960s [24]. Various CMCs have used this process for the formation of matrixes. By reacting gaseous precursors with solid ceramics, the CVI process produces solid ceramics. SiC and UHTCs can be formed in the following ways (TiB_2, HfC, etc.):

$$CH_3SiCl_3(g) + \text{excess } H_2(g) \rightarrow SiC(s) + 3HCl(g) + \text{excess } H_2(g) \quad (3)$$

$$TiCl_4(g) + 2BCl_3(g) + 5H_2(g) \rightarrow TiB_2(s) + 10HCl(g) \text{ (at 900 °C)} \quad (4)$$

Stoichiometric compounds can be prepared using the CVI method. While this method has a longer processing time, it is much more efficient than the other methods [21, 24].

3.3. Precursor infiltration and pyrolysis (PIP)

Using the PIP process, carbon fiber composites can be introduced with UHTC matrix by injecting a precursor with low viscosity into porous composites or fiber preforms, followed by high-temperature pyrolysis [31, 32]. Pyrolysis at high temperatures can lead to metal carbides, borides, or nitrides, which are normally metal-containing polymers. There will always be several cycles of infiltration and pyrolysis

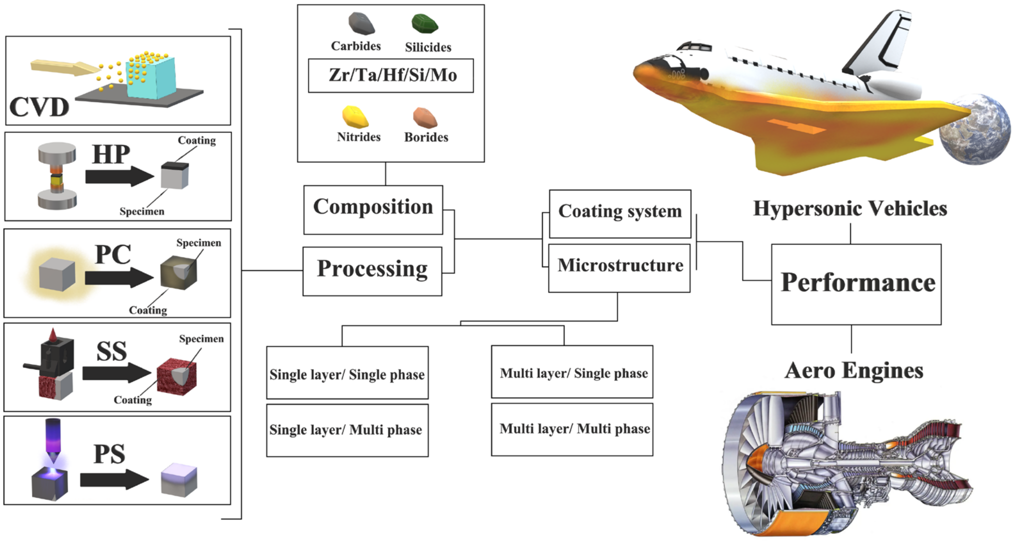

Fig. 1. UHTC applications, coatings, and some processing methods (inspired by Ref. [46]).

required to reach the desired density [33]. With this technique, it is possible to introduce various ceramics at the same time and achieve a production close to a net shape. In comparison with CVI, this method is cheaper, has a shorter preparation period, and allows for greater infiltration. At the same time, the maximum pyrolysis temperature is always below 1500 °C, and heat treatment usually causes less damage to carbon fiber compared to the reactive melt infiltration process (please see the next section). Its main disadvantage is the matrix is easily prone to shrinking over pyrolysis, leading to pores and cracks [34, 35].

3.4. Reactive melt infiltration (RMI)

By reacting mixtures of molten metal with substrates containing B or C at elevated temperatures, RMI can also introduce carbides or borides matrix into the composites [16]. A ceramic matrix element with a low melting point can be used for this process when it readily wets fibers. Because macroscopic porosities in the composite may be quickly filled to get a uniformly infiltrated dense composite, the technique is more affordable and more effective than CVI and PIP [32, 36]. In addition, this method allows for multiple metals or compounds to be added simultaneously to the reacting mixtures to provide various matrixes for the composites. RMI is also capable of fabricating components with complex geometries. However, a composite's mechanical properties may be damaged during fabrication due to unavoidable reactions of molten metal with carbon fibers. Also, residual metal is likely to be left behind, where it may melt at elevated temperatures and speed up creep or attack constituent phases, decreasing material performance as a result [24, 32]. Composites of C/C–ZrC materials are usually formed by RMI after metallic zirconium, or intermetallic compound of Zr is reacted with a porous C/C skeleton. The same process can be used to manufacture SiC–ZrC matrixes by reacting porous carbonates with powdered Si and Zr or with an intermetallic compound containing Zr and Si; a UHTC boride matrix may also be added to the composites via combining Zr–B alloy with porous carbonate or Zr with porous carbonate–B_4C [37].

3.5. Slurry infiltration (SI)

Slurry infiltration involves infiltrating UHTC powders into fiber preforms using a fluid (aqueous or organic) as the matrix precursor, which can be pressureless or pressure-assisted [37]. The CVI, PIP, or other routes can be used to densify preforms containing UHTC particles to add ceramic matrix or carbon matrix into the UHTC–carbon fiber preforms. UHTCs can be introduced into composites using this process at a much lower cost and, depending on the requirements of the material's application and design; UHTCs are also available in different compositions and quantities. Anyway, particle agglomeration may block the outer layer pores of the preforms, causing successive densification to be difficult [38, 39].

3.6. Sol-gel

Fine ceramics are synthesized with sol-gel by hydrolyzing, condensation gelating gradually, and post-treating with inorganic or organic materials to obtain oxides or other compounds. UHTC matrix composites have been manufactured using this method recently [40]. A porous carbon–boron carbide matrix, impregnated in a three-dimensional carbon fiber preform, was prepared via pyrolyzing and carbothermally reacting PVA and H_3BO_3 as gel precursors. Finally, the ZrB_2–ZrC–SiC matrix was formed by chemically reacting the C–B_4C matrix with molten $ZrSi_2$ [39]. Combining the processes discussed previously can be employed to enhance the fiber preforms densification or to improve the properties of composites on the basis of their advantages and disadvantages [41, 42].

4. UHTC coatings

A coating is another application for UHTCs in addition to bulk ceramics and composites. At ultra-high temperatures, UHTC coatings protect substrates from oxidation and ablation [38]. Fig. 1 shows UHTC applications, coatings, and some processing methods. The ideal temperature for each UHTC depends on its composition, and usually, it is combined with a silicide (SiC, $MoSi_2$, etc.) [43]. By adding UHTC to silicides, the silicon-based traditional ceramic coatings are able to overcome their deficient oxidative ability at high temperatures or low oxygen partial pressures. The preparation of UHTC coatings can be accomplished via multiple methods, such as pack cementation (PC), CVD, slurry sintering (SS), plasma spray (PS), and HP [44]. As a result, the UHTC coatings selection is significantly influenced by the composition and physical properties of the aimed application (aero-thermochemical demand) and the processing techniques (feasibility of the fabrication routes, specific shaping availability, and cost) [45]. The coating structure design needs to take into account not only the above design rules for UHTC coatings, but also the multiphase synergistic protection, the interfacial compatibility design, multiple processing routes, and multiscale toughening [46]. These coatings are ideal for turbine blades, rocket engine nozzles, and hypersonic vehicle thermal protection systems (TPS) since they have high melting temperatures, and excellent resistance to oxidation and ablation [47, 48].

5. Conclusions

The main ingredients of UHTCs are nitride, carbide and boride compounds consisting of transition metal elements in group IVB of the periodic table. Despite the sturdy covalent structure, UHTCs maintain exceptional mechanical properties, ultra-high melting points, and withstand ablation at excessive temperatures. Manufacturing advanced engineering composites makes UHTCs perfect candidates for structural functions in rockets and hypersonic automobiles that require intense environments. Different processing routes are reachable for fabricating composites from gaseous or liquid precursors, slurries, and solids. Bulk UTHCs are commonly characterized with the aid of low fracture longevity and terrible resistance to thermal shock, which limits their direct utility to main edges and propulsion structures as exterior thermal safety systems. UHTCs are nevertheless unable to meet engineering necessities regardless of having been toughened with particles, whiskers, carbon nanotubes, and graphene. Ceramic matrix composites with fiber-bolstered coatings are developed as the most important utility structure for UHTCs for basically addressing the intrinsic brittleness of bulk ceramics. UHTC processes, compositions, and microstructures, as properly as properties, mechanisms, and coating techniques are mentioned in this brief review.

CRediT authorship contribution statement

Farrokhfar Valizadeh Harzand: Conceptualization, Writing – original draft.
Sahar Anzani: Resources, Writing – original draft.
Aziz Babapoor: Supervision, Writing – review & editing.

Data availability

The data underlying this article will be shared on reasonable request to the corresponding author.

Declaration of competing interest

The authors declare no competing interests.

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