

ULTRA-HIGH-TEMPERATURE CERAMIC MATERIALS MODIFIED BY GRAPHENE: AN OVERVIEW

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Ultra-high-temperature ceramics (UHTCs) are materials capable of withstanding temperatures above 2000 °C while maintaining exceptional properties, making them ideal for aerospace, automotive, and energy applications. However, they face challenges such as brittleness and limited oxidation resistance. This review highlights the potential benefits of modifying UHTCs with graphene, a material known for its excellent mechanical, thermal, and electrical properties. Incorporating graphene into UHTCs can enhance their mechanical properties, improve the oxidation resistance, increase the thermal conductivity, and tailor the electrical properties, while also improving the processability. By addressing the inherent limitations of UHTCs and enhancing their properties, graphene-modified UHTCs show promise for a wide range of high-temperature applications. The review covers recent research achievements in graphene/UHTCs composites, focusing on the synthesis methods, microstructures, macroscopic mechanical properties, oxidation resistance, thermal shock resistance, and the underlying mechanisms.

INTRODUCTION

Ultra-high-temperature ceramics (UHTCs) are an exceptional class of materials known for their ability to withstand extremely high temperatures, typically above 2000 °C while maintaining exceptional mechanical and physical properties [1]. These materials, composed of metal carbides, borides, and nitrides, have gained significant attention in recent years due to their unique properties, which make them ideal candidates for a wide range of high-temperature applications in the aerospace, automotive, and energy industries [2]. The remarkable properties of UHTCs can be attributed to their strong covalent bonds and unique crystal structures. UHTCs possess high melting points, excellent chemical stability, and outstanding wear, corrosion, and oxidation resistance [3]. These characteristics make them suitable for use in extreme environments where conventional materials would fail. Additionally, UHTCs exhibit high thermal conductivity, low thermal expansion coefficients, and good electrical conductivity [4]. Their ability to retain strength at elevated temperatures is crucial for applications that require structural stability under extreme heat.

Some of the most common UHTCs include zirconium diboride (ZrB_2), hafnium diboride (HfB_2), and tantalum carbide (TaC) [5-7]. Researchers have extensively studied these materials, as well as others, to better understand their properties and to optimise

their performance for specific applications. However, despite their impressive properties, UHTCs still face certain challenges, such as brittleness and limited resistance to oxidation at ultra-high temperatures [8]. These limitations also include difficulties in processing [9]. Consequently, there is a growing need for modifying UHTCs to overcome these challenges and optimise their performance for specific applications [10].

Graphene, a single layer of carbon atoms arranged in a hexagonal lattice, is known for its exceptional mechanical, thermal, and electrical properties. It has a high specific strength, remarkable flexibility, and extraordinary thermal and electrical conductivity. These characteristics make it an attractive candidate for modifying UHTCs to improve their overall performance. The incorporation of graphene as a secondary phase in UHTCs can potentially address their inherent limitations, such as brittleness and oxidation resistance, while preserving their desirable properties. The need for modifying UHTCs with graphene arises from the following considerations:

1. Enhanced mechanical properties: UHTCs are known for their brittleness, which can limit their application in load-bearing components. The addition of graphene can help mitigate this issue by improving the fracture toughness and ductility of the ceramic matrix. This is due to graphene's high strength, flexibility, and ability to deflect cracks, thus enhancing the overall mechanical properties of the composite.

2. Improved oxidation resistance: UHTCs tend to oxidise at ultra-high temperatures, which can compromise their structural integrity and limit their service life. Graphene, with its excellent thermal stability and barrier properties, can effectively protect the ceramic matrix from oxidation, enhancing the material's resistance to high-temperature degradation.

3. Increased thermal conductivity: The addition of graphene can improve the thermal conductivity of UHTCs, which is essential for effective heat dissipation in high-temperature applications. The high thermal conductivity of graphene can facilitate the efficient heat transfer within the composite material, reducing the thermal gradients and thermal stress.

4. Tailored electrical properties: Graphene-modified UHTCs can exhibit tunable electrical properties, allowing for the design of materials with desired electrical characteristics. This can be particularly useful for applications such as high-temperature sensors, electrical contacts, and energy storage devices.

5. Improved processability: The presence of graphene can enhance the processability of UHTCs by promoting densification during sintering and reducing grain growth. This can lead to the fabrication of materials with a refined microstructure, improved properties, and reduced processing costs.

The need for modifying UHTCs with graphene stems from the desire to overcome their inherent limitations and further enhance their exceptional properties. The incorporation of graphene can significantly improve the performance of UHTCs, making them more suitable for a wide range of high-temperature applications in the aerospace, automotive, and energy industries. By understanding the benefits of graphene modifications, researchers can explore new avenues for the development of advanced materials with superior performance and broad applicability. In this review, we provide a comprehensive overview of the recent research achievements in the field of graphene/UHTC composites, both domestically and internationally. We focus on the synthesis methods, microstructures, macroscopic mechanical properties, oxidation resistance, thermal shock resistance, and the underlying mechanisms of these composites. In particular, we discuss the role and mechanisms of graphene in enhancing the toughness of UHTCs. Furthermore, we address the challenges faced by this field and provide insights into future developments.

EXPERIMENTAL

Synthesis Methods

Selecting an appropriate fabrication process is crucial for achieving the desired structure and performance of the composite material. Currently, graphene/UHTC composites are primarily produced

through powder sintering densification processes, which involve preparing graphene/UHTC composite powders and then sintering them to obtain dense bulk composite materials. This method offers simplicity, good material properties, and easily adjustable parameters, making it the preferred technique for preparing most graphene/UHTC composites.

First, graphene is dispersed in a liquid phase to create a stable graphene suspension. Then, mechanical mixing methods, such as ball milling, magnetic stirring, or ultrasonic dispersion, are employed to directly mix the graphene with the ceramic powder, followed by drying to obtain the composite powder [11]. For instance, graphene nanoplatelets were dispersed in ethanol using an ultrasonic treatment [12]. Subsequently, SiC_w and ZrB₂ powder mixtures were added to the graphene-based suspensions, followed by an additional 20 min of ultrasonic blending. The resulting suspensions were then dried using a hot plate magnetic stirrer. The dried powder mixtures were sieved through a 100-mesh screen and finally poured into a graphite mould coated with BN powder and a dual-layer graphite foil. In a study by Nieto et al. [13], the received graphene powders were subjected to 90 minutes of ultrasonication in acetone to reduce the agglomeration. The graphene powder was then combined with a TaC powder and ultrasonicated. As a reference sample, a pure TaC powder was also treated with ultrasonication. Afterward, the TaC-graphene-acetone mixture was placed in an oven at 75 °C for 24 h to dry. The dried powders were then ground and returned to the oven for an additional 24 h.

Densification sintering is a critical process step for obtaining ceramic composite materials, as it significantly influences the material's microstructure and macroscopic properties. The primary sintering techniques include pressureless sintering (PS) [14-17], hot isostatic sintering (HIP) [18-20], hot pressing (HP) [21-25], and spark plasma sintering (SPS). Hot pressing (HP) is characterised by the simultaneous application of heat and pressure to form and sinter ceramic materials. Nevertheless, due to the sintering mechanism constraints, the heating rate and sintering pressure for the HP method cannot exceed 15 °C·min⁻¹ and 30 MPa, respectively [26]. Conversely, the SPS method allows for a heating rate and sintering pressure of up to 100 °C·min⁻¹ and 70 MPa, respectively [27]. Ceramic materials fabricated using SPS demonstrate significantly enhanced properties compared to those produced via HP. This can be primarily attributed to the higher heating rates and sintering pressures employed in SPS, which result in a smaller grain size than that of HP-sintered materials. Consequently, SPS is a more suitable approach for the preparation of ceramic materials.

Among the various sintering techniques, SPS is the most widely used for fabricating graphene/ultra-high-temperature ceramic composites due to its rapid sintering rate and the high density of the resulting

samples [28–35]. The short sintering time of SPS has been proven to be beneficial for preserving the graphene structure [36]. The introduction of graphene can cause ceramic particle rearrangement during the initial sintering stage, and its wrapping mechanism can significantly inhibit grain growth. In the later sintering stage, the carbon structure of graphene [37] can serve as a sintering aid. Additionally, graphene can enhance the electrical conductivity and thermal conductivity of ceramic powders, leading to more uniform heating during the SPS process [38]. Figure 1 shows images of ZrB_2 and ZrB_2 -GNP sintered pellets prepared by SPS [39]. Asl and colleagues [40] performed a Transmission electron microscopy (TEM) analysis on spark plasma sintered ZrB_2 -SiC-graphene nanocomposites. Their findings contradicted previous reports, indicating that graphene nano-platelets might not be involved in the reactive sintering process, especially when employing SPS as a fabrication technique. It was proposed that the carbon diffusivity and concentration gradient could influence the formed interfaces.

Moreover, lasers can effectively alter the coating's surface to control the microstructure, decrease the porosity and surface roughness, and enhance durability. Laser micromelting is mainly affected by the laser sintering parameters, the laser beam's optical properties, and the photothermal-mechanical characteristics of the treated substrate. Thermal residual stress, microcracks, and increased material loss result from the melting and sputtering of materials due to the laser thermal energy absorption. Some researchers have examined the influence of laser parameters on the mechanical, thermal, and tribological properties of UHTCs treated with lasers. Wang et al. [41] investigated MCrAlY coatings applied by plasma spraying and subsequently remelted with a CO_2 laser. Post-laser remelting, the layered structure vanished, the density increased, and defects, such as the porosity and inclusions, were virtually eliminated, leading to an improved thermal corrosion performance. Lin et al. [42] examined the pulsed laser ablation of bulk TaC substrates

in a vacuum environment using high power and nano-second pulses for potential tribological applications, noting that the refractory particles' bimodal minimum band gap appeared beneficial. In a study incorporating graphene, Liu et al. [43] explored the effects of laser parameters on the microstructure and properties of plasma-sprayed yttrium oxide coatings applied to a graphite matrix.

RESULTS AND DISCUSSION

Properties of Graphene-Modified UHTCs

Graphene nanoplatelets have garnered significant interest due to their ability to enhance the mechanical properties of UHTC materials through various mechanisms. The early research primarily focused on the toughening effect of graphene on the UHTC matrix. Numerous studies have demonstrated that the introduction of graphene increases the uniformity and density of the pressed parts, while the graphene wrapping mechanism significantly suppresses grain growth. This intrinsic mechanism, coupled with the interactions between the graphene nanoplatelets and the grains, leads to a crack suppression mechanism. Microstructural observations reveal phenomena such as crack deflection and crack bridging, ultimately resulting in the toughening effect on the UHTC matrix. For instance, hybrid ZrB_2 -based UHTCs with relative densities exceeding 99.7 % were produced using vacuum spark plasma by incorporating 25 vol. % SiC whiskers and 0 – 7.5 wt. % graphene nanoplatelets [12]. The ZrB_2 -GNP-SiC_w nanocomposites displayed inhibited grain growth compared to ZrB_2 -SiC_w UHTC without graphene. Yang et al. [44] enhanced the ZrB_2 -25 vol. % SiC ceramic material by adding 5 wt. % graphene with an average particle diameter of 4 – 12 μm and an average particle thickness of 2 – 18 nm. Graphene powder was dispersed in ethanol using ultrasonication, followed by the addition of ZrB_2 and SiC powders to the resulting dispersion. After drying, grinding, and hot pressing



Figure 1. Images of sintered pellets of ZrB_2 and ZrB_2 -GNP composites. Reproduced with permission from Ref. [39].

at 1850 °C (1 h) and 20 MPa, the ceramic material achieved a density of 99.1 % and increased hardness and fracture toughness values. The researchers observed that the toughening resulted from the crack deflection, crack branching, and graphene flake pull-out. Furthermore, it was found that graphene particles in the manufactured ceramics were significantly agglomerated.

Yadhukulakrishnan et al. [37] and Asl et al. [45] also chose to toughen the ZrB₂ ceramic system by incorporating graphene, obtaining composite materials with high densities up to 97 % and near-full density (> 99 %), respectively. In terms of the mechanical properties, the fracture toughness and flexural strength of the system showed significant improvements, highlighting the prominent reinforcing effect of graphene, which can be attributed to its crack deflection and crack bridging toughening mechanisms. Similar research has also been confirmed in the TiB₂ system [46] and TaB₂ system [34], where basal-oriented TiB₂ can nucleate on a graphene template, forming oriented crystal growth mechanisms. All of the aforementioned studies have identified the same trend: graphene nanoplatelets in the system effectively hinder the grain growth of the matrix, and, as the amount of graphene added increases, the density of the composite material continuously improves. This is due to the elimination of oxide impurities and the formation of favourable phases through interface reactions induced by the graphene nanoplatelets, thus promoting densification of the composite material. Upon observing the microstructure, it has been discovered that the toughening of the composite material is achieved through the wrapping, pull-out, crack deflection, and crack bridging of the graphene nanoplatelets. However, if the amount of graphene added is excessive, the uneven distribution of the graphene nanoplatelets in the system may lead to agglomeration behaviour, resulting in a decrease in both the density and hardness of the composite material.

In a work that aligns with this ideology [47], SiC whiskers were employed to achieve a synergistic effect with the silicon-containing component, where the GO content in the initial composite powders was raised to 5 and 10 vol. %. Hot pressing was performed as previously described [36], yielding ceramic samples with slightly lower densities of 98.5 % (5 vol. % GO) and 99.3 % (10 vol. % GO). Elevating the graphene content from 5 to 10 vol. % resulted in a reduction in both the flexural strength and fracture toughness, which was also ascribed [47] to the agglomeration of graphene flakes during the hot pressing process. It was observed that when the GO content exceeded 20 vol. %, the mechanical properties of the fabricated composite materials further deteriorated. At the fracture site of ceramic composite materials, the crack bridging and pull-out of graphene nanoplatelets promote the crack propagation in the re-

inforced composites. Other studies have found that, regardless of different processing methods and matrix systems, the fracture toughness exhibits a linear increasing trend with an increase in the amount of nano-graphene used [12, 48]. This further confirms that graphene nanoplatelets wrap around ceramic particles, inhibiting grain growth, with the primary toughening mechanisms being crack bridging, crack arresting, and crack deflection.

The mechanical properties of the hetero-interface are crucial to the performance of graphene-reinforced composites. Zhang et al. [49] sandwiched graphene between two stable layers, constructing 12 interfacial models on the ZrB₂ surface and systematically studied the structure, adhesion, cleavage, and sliding of the hetero-interface between the ZrB₂ matrix and the graphene nanoplatelets using the density functional theory. The results were compared with the existing experimental data. It was shown that the surface chemical properties of the ZrB₂ matrix material largely determine the nature of the interface structure and interfacial interactions. The interfacial bonding mechanisms of the two interface types are different: Zr-C interfaces exhibit strong chemical bonding, resulting in higher resistance to crack propagation and interfacial sliding capabilities. Their response to mechanical stress is significantly affected by the wrinkling of graphene; whereas B-C interfaces, through weaker π - π stacking interactions, are more prone to interfacial debonding and shear deformation, exhibiting characteristics similar to those of two-dimensional material heterostructures.

Yadhukulakrishnan et al. [37] demonstrated that as the graphene content increased from 2 vol. % to 6 vol. %, the fracture toughness of ZrB₂-graphene ceramics gradually increased. When the graphene content in ZrB₂ increased to 6 vol. %, the fracture toughness of ZrB₂-6 vol. % graphene increased from 1.51 MPa·m^{-1/2} to 2.77 MPa·m^{-1/2}. Asl et al. [45] added 5 wt. % graphene nanoplatelets to ZrB₂-25 vol. % SiC materials, increasing the fracture toughness from 4.3 MPa·m^{-1/2} to 6.4 MPa·m^{-1/2}. Zhang et al. [50] added 5 vol. % GO to ZrB₂-20 vol. % SiC materials, resulting in an increase in the fracture toughness from 4.20 MPa·m^{-1/2} to 7.32 MPa·m^{-1/2}. In ZrB₂-SiC ceramic composites without graphene nanoplatelets, cracks exhibited linear crack propagation along with intergranular fractures and transgranular fractures. When cracks propagated in ZrB₂-20 % SiC-2 % graphene ceramic materials, graphene bridging was observed in the cracks, and crack deflection was common after crack propagation. The toughening mechanisms of ZrB₂-SiC-graphene ceramic materials were attributed to the graphene bridging, pull-out, and crack deflection. From a "bottom-up" assembled graphene/ZrB₂-SiC micro-macro laminated structure, ZrB₂ ceramic particles were observed to be uniformly distributed in a continuous multilayer graphene network [51]. After densification

by the SPS method, alternating compressive and tensile layers were formed in the graphene/ceramic composites, further enhancing the fracture toughness of the composites. The composites also exhibited high strength and high toughness, with a fracture toughness more than twice that of non-laminated structures. Furthermore, in hierarchical structures [52] and large-pore graphene network structures [53], graphene formed a three-dimensional continuous network within the matrix and created weak grain boundaries and optimal thermal conduction pathways within the composites, significantly enhancing their toughness. The intrinsic mechanism involved graphene sheets exhibited crack bridging, pull-out, branching, deflection, and other phenomena within the matrix, releasing the interfacial stress at the grain boundaries, hindering creep deformation, and thus enhancing the macroscopic performance of the composites. In the dual-composite "brick-mortar" ceramic structure, Cheng et al. [54] proposed constructing dual-composite isotropic structures to obtain isotropic, weak-interface toughened ZrB₂-SiC ceramics as an ideal method. In this system, ZrB₂-SiC-graphene acted as a weak interface, achieving the multiscale toughening of ZrB₂-SiC ceramic materials. Subsequently, they prepared in-plane isotropic non-axially aligned ZrB₂-SiC/ZrB₂-SiC-graphene short-fibre single-crystal ceramics and continuous fibre single-crystal ceramics [55, 56]. This series of studies demonstrated that not only did the density and fibre diameter have a significant impact on the microstructure and performance of fibre single-crystal ceramics, but the fibre sheet arrangement angles also affected the microstructure and macroscopic properties of fibre single-crystal ceramics. Xia et al. [12] fabricated hybrid zirconium diboride ceramics consisting of silicon carbide whiskers (SiC_w; 25 vol. %) with varying concentrations of graphene nano-platelets (0–7.5 wt. %). A significant improvement in the fracture toughness was observed, following a linear pattern, as the graphene nano-platelets content increased from zero to 7.5 wt. % in the nano-graphene doped specimen. The principal toughening mechanisms identified were crack bridging, crack halting, and crack deviation.

Graphene possesses exceptional electrical and thermal properties, with a room temperature electron mobility of approximately $1.5 \times 10^4 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and a thermal conductivity as high as $5.3 \times 10^3 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ [57]. In ultra-high-temperature ceramic materials, the introduction of graphene increases the thermal conductivity of the matrix material, accelerating the heat dissipation in localised overheating regions, thereby prolonging the service life of the material. During the composite formation process between the graphene and the ceramic matrices, graphene creates a thermal interface and establishes a three-dimensional high heat transfer pathway. As a result, it can serve as an excellent thermal interface material to enhance the thermal conductivity and thermal diffusivity of matrix materials. Furthermore, the addition

of graphene introduces additional effective phonon transport pathways, leading to an increase in the thermal conductivity with the increasing graphene content.

Yang et al. [58] highlighted the distinct characteristics of electrostatic interactions in a suspension of GO particles mixed with ZrB₂ and SiC particles, which possess opposing surface charges. This enabled the creation of more stable dispersions and ensured the uniform distribution of the components within the bulk of the ZrB₂-20 vol. % SiC-(0–3) wt. % CG ceramic materials. It was observed that the thermal conductivity of the optimal composite, containing 2 wt. % graphene, surpassed that of the unmodified composite by 42 %. The combination of high fracture toughness and elevated thermal conductivity resulted in the produced samples exhibiting exceptional thermal resistance.

Simonenko et al. [59] obtained similar results in the HfB₂-30 % (volume fraction) SiC material system by introducing 2 % graphene. The overall thermal conductivity of the composite material increased from $113 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ to $164 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, an improvement of approximately 45 %. Chen et al. [60] also confirmed, in their study on ZrB₂-SiC/graphene composite materials, that the introduction of graphene significantly enhances the ceramic matrix's thermal diffusivity, thermal conductivity, and specific heat capacity. However, any excessive addition can lead to a decline in the composite material's thermal conductivity. This is attributed to the agglomeration phenomena that reduce graphene's intrinsic thermal conductivity and is accompanied by a decrease in the ceramic matrix grain size and an increase in porosity.

Enhancing the mechanical properties of UHTC matrices is crucial for their practical engineering applications. Furthermore, the oxidation resistance of UHTCs is of vital importance. Under high enthalpy supersonic flight conditions, novel spacecraft are subjected to severe thermo-mechanical-oxidative coupling effects, leading to erosive damage in the UHTC materials. This results in significant mechanical spalling on the material surface, reduced structural integrity, and a weakened overall strength. Consequently, improving the oxidation behaviour is an essential research direction for UHTC materials under extreme environmental conditions. Graphene's high thermal conductivity, when introduced into the ceramic matrix, significantly reduces the thermal gradient in the composite material exposed to plasma flow, leading to a substantial increase in the thermal conductivity. This enhancement allows for better heat diffusion and conduction, avoiding localised overheating. Furthermore, graphene wraps around and intertwines between grains, making oxygen diffusion through grain boundaries difficult or even "sealing" the oxidation grain boundaries and diffusion pathways. The toughening effect of graphene also inhibits the generation and propagation of cracks, thereby

preventing any rapid oxygen penetration. Crack suppression is crucial for impeding oxidation rates. In addition to the physical mechanisms mentioned above, graphene also consumes oxygen through chemical reactions, weakening the oxygen's erosion on the ceramic matrix and providing a protective effect, thereby enhancing the oxidation resistance of the ceramic matrix. In carbide ceramic systems, graphene also serves as a carbon source needed to reduce oxides to carbides, suppressing the formation of oxide layers through a localised reduction.

Graphene's inclusion has been demonstrated to improve the oxidation resistance of TaC-graphene composites when exposed to high-temperature plasma flow [61]. Through several distinct graphene mechanisms, the oxide layer thickness formation is reduced by up to 60 %. Graphene's high thermal conductivity enables the heat distribution throughout the sample, diverting it from the front surface subjected to the most extreme conditions. Graphene's toughening effect allows the composites to withstand cracking due to thermal shock, chemical assault, and high-speed plasma flow. Preventing cracks is crucial for reducing oxidation rates, as cracks facilitate rapid oxidation penetration. A graphene grain sealing mechanism is suggested, where graphene seals the grain boundaries, obstructing any oxygen influx. The remaining graphene also creates localised reducing environments by supplying the excess carbon necessary for converting the formed oxide, Ta₂O₅, to TaC. Graphene's oxidation resistance mechanisms also safeguard the unoxidised underlying structure from structural damage. Graphene's inherent toughening, grain sealing, and thermal conductivity mechanisms could potentially be applied to other ultrahigh-temperature ceramic systems.

The oxidation behaviour of HfB₂-30 vol. % SiC UHTC containing 1 vol. % of RGO was investigated during exposure to a supersonic dissociated air jet [59]. The heat fluxes ranged between 363–779 W·cm⁻²,

and the total exposure duration was 2000 s. Although the incorporation of a relatively small quantity of reduced GO (1 vol. %) did not prevent a significant increase in the average surface temperature to 2300–2400 °C, the duration of surface temperatures below 1800–1850 °C substantially increased. This is likely attributed to the enhanced thermal conductivity in the ceramic material. The material's ablation rate was found to be 6.5×10^{-4} g·cm⁻²·min⁻¹, a value that lies between the rates for HfB₂-SiC ceramics and those doped with 2 vol. % graphene. The long-term oxidation resistance of UHTC (HfB₂-30 vol. % SiC)-2 vol. % RGO (Figure 2) under supersonic airflow exposure has been investigated [62]. The surface temperature of graphene-modified ceramics, heated by high-enthalpy airflow (heat flow q reached 779 W·cm⁻²), did not surpass 1700 °C, which is 650–700 °C lower than HfB₂-30 vol. % SiC baseline ceramics. This might be attributed to the enhanced efficiency of heat transfer from the sample to the water-cooled module due to the higher thermal conductivity of the RGO-containing material. Consequently, a reduction in the material degradation degree was observed, with a decrease in the recession rate and a reduction in the overall oxidised ceramic layer thickness by a tenth. The distinct microstructure of the oxidised surface and near-surface region upon aerodynamic heating of the graphene-modified ceramic material was demonstrated.

Future prospects and research directions

Graphene's uniform dispersion in UHTC matrices has been proven to significantly enhance and toughen the materials, while also improving the composite's oxidation resistance and thermal shock resistance to a certain extent. However, the overall application of graphene in ceramic materials is still in its infancy, with numerous issues requiring in-depth investigation.

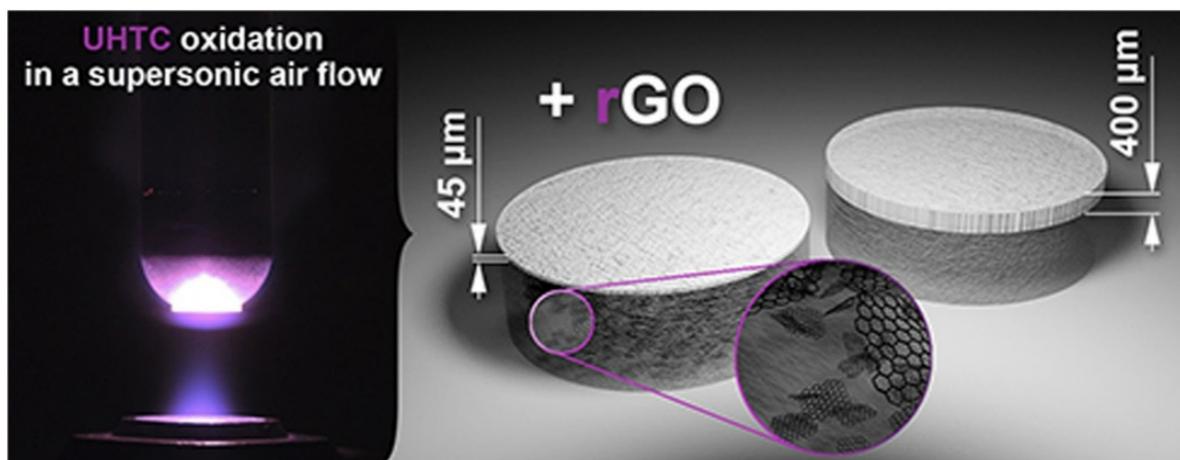


Figure 2. Oxidation of graphene-modified HfB₂-SiC ceramics by supersonic dissociated air flow. Reproduced with permission from Ref. [62].

Firstly, the challenge of uniformly dispersing graphene in the ceramic matrix arises due to the strong chemical intercalation and weak van der Waals interactions between the two phases. When the graphene content increases, the agglomeration issue becomes more severe, leading to a decline in the mechanical, electrical, and thermodynamic properties of the composite material. To maximise its positive effects, achieving effective dispersion of graphene and an appropriate interface bonding between the matrix and graphene is crucial. Chemical methods, such as the in-situ polymerisation and functionalisation, can be employed to enhance graphene dispersion, as well as physical methods like adding dispersants, promoting charge attraction, and mechanical mixing.

Secondly, the manufacturing and processing of UHTC materials can easily introduce defects, which significantly impact the macroscopic properties of the composite material. At present, there is limited research on the mechanisms behind the changes in graphene itself during the sintering process and its influence on controlling the ceramic matrix grain sizes. The sintering process often involves plasma sintering, and future research should explore alternative sintering techniques, such as low-temperature densification, and investigate microstructure control methods.

Moreover, the study of graphene's role in enhancing the matrix oxidation resistance and thermal shock resistance is still scarce and superficial, with multiple mechanisms working together not yet fully understood. There are numerous unknown mechanisms that need exploration and practical application problems need to be overcome. However, this research is vital for understanding graphene's role in the system and further optimising its performance. In particular, the interface between ceramics and graphene remains unclear. Further research is needed to investigate the interface adhesion fracture energy, its dependence on the crack growth rate and temperature, and the influence of the processing temperature and environment on interface adhesion fracture energy. Significant potential remains for streamlining the microstructure simulation, ranging from the model creation to the actual simulation process. The secondary development of computer-aided engineering (CAE) software, in conjunction with programming tools, is expected to have a substantial impact on both practical applications and scholarly research.

CONCLUSIONS

In recent years, graphene/UHTC composites have sparked interest in the materials science community, as graphene's exceptional properties hold great potential for expanding the applications of ceramic materials. In this review, we examined the manufacturing techniques, fracture resilience, heat conduction, and degradation performance (in oxidative environments)

of graphene/UHTC composites. The production of these composites is achieved through HP, HIP, PS, and SPS methods, each with their own strengths and weaknesses in terms of the processing duration, operating temperatures, and composite porosity. Numerous investigations have been conducted to enhance these procedures. Graphene achieves toughening effects on UHTC matrices through phenomena such as grain wrapping, crack deflection, and crack bridging. It inhibits the oxidation process of the matrix through physicochemical coupling effects while further improving the mechanical and thermal properties of the ceramic matrix, enhancing its thermal shock resistance. The fracture resistance of graphene/UHTC composites is heightened with the inclusion of graphene. To boost the fracture resilience of these materials, a weak interphase must be created, as it enables crack deflection at the interface, preventing the simultaneous fracturing of both graphene and the matrix. The thermal conductivity of these composites in the through-the-thick direction declines as the graphene volume fraction increases, due to the interface between graphene and the matrix acting as a thermal conduction barrier. From the analysis thus far, it can be concluded that graphene/UHTC composites based on Zr or Hf demonstrate exceptional ablation properties in oxidative environments at temperatures above 2000 °C. The mechanical behaviour and thermal conductivity of these composites can be adjusted by altering the graphene volume fraction. Of course, the current research in this area remains relatively limited, and many questions need to be addressed and further explored, making the scientific work in this field of great practical significance. It is believed that as research progresses, the application scope of graphene-enhanced UHTCs will broaden, and their reliability will be further improved.

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