ceramics

Review

Superior Ceramics: Graphene and Carbon Nanotube (CNT) Reinforcements

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Abstract: Carbon nanotube (CNT)/graphene ceramic composites with outstanding properties are expected to replace a number of components currently used in the automotive and aerospace industries in the future. Consequently, this area of research has progressed significantly. This review paper, therefore, delves into the enhancement of ceramic properties through the integration of graphene and CNTs. These reinforcements are known to mitigate the inherent brittleness of ceramics, thereby unlocking their potential for applications in sectors requiring high mechanical reliability, such as the aerospace, automotive, and biomedical industries. By summarizing recent research, this paper outlines various preparation methods, including ball milling, heat pressing and spark plasma sintering, and discusses how these techniques contribute to improved mechanical and thermal performance. This review emphasizes the critical role of graphene and CNT ratios, sizes, and their synergistic effects in enhancing fracture toughness, machinability, and overall structural integrity. Thus, this paper provides a comprehensive overview of the current research in this area and discusses the potential of these technologies.

Keywords: ceramic reinforcement; graphene; carbon nanotubes (CNTs); nanomaterials

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1. Introduction

Ceramic engineering materials are greatly recognized for their superior mechanical properties: stiff, strong, and hard, with good wear resistance, good thermal properties regarding high-temperature resistance and properties of insulation at the same time [1,2]. All these unique characteristics of ceramics, including being lightweight, make them highly corrosion-resistant and chemically stable [3]. In addition, they offer potential applications in a wide range of industrial sectors. Engineering ceramics have become generally adopted within the most critical industries over the last few decades, as, under extreme conditions, these materials are able to maintain their properties. For instance, in batteries because of the stability under high loads; insulation in electronics; and in thermal and mechanical parts thanks to the resistance to wear and functioning at elevated temperatures [4]. Ceramics are also employed in various automotive components, such as oxygen sensors, knock sensors, and braking systems, due to their strength and reliability [5,6]. Their tolerance for high temperatures and hostile environments also makes them suitable for use in the aerospace industry. They are used for structural members in hot structures and thermal protection systems [7]. With all these assets, there are enormous drawbacks that cannot allow more substantial and wider use of ceramics. Their intrinsic brittleness, difficulty in machining, and high production costs are major drawbacks to their application in more varied fields [8]. These disadvantages are particularly disturbing in areas where mechanical reliability and performance are not considered.

Thus, to overcome these difficulties, researchers have developed ceramic composites that include a wide range of reinforcing materials. Some of these reinforcements include fibers, particles, or whiskers that increase the toughness of ceramics through processes like crack deflection, bridging, and pull-out [9,10]. Additionally, advanced processing, such as hot pressing and spark plasma sintering, further improves ceramics' microstructure, leading to much better mechanical performance and reliability [11–13].

Strengthening ceramics to eliminate their inherent brittleness is crucial for their wide use in demanding applications in sectors including aerospace, automotive, and biomedical engineering. An increasingly common method of improvement of ceramics is the addition of graphene and carbon nanotubes (CNTs) to ceramic matrices. Graphene and CNTs have received great attention due to their unique mechanical, thermal, tribological and electrical properties [14–17]. In combination with ceramics, they are known to significantly enhance toughness and fracture resistance, thus eliminating the brittleness commonly limiting ceramic applications. Furthermore, these composites demonstrate improved machinability and thermal stability, making them more amiable for use in complex, high-performance service.

Graphene is known for its high strength and fracture toughness [15], while CNTs offer a high aspect ratio and superior mechanical properties [14]. Together, they serve to enhance crack deflection and distribute stress more homogeneously within the ceramic matrix, which result in composites with significantly better toughness and durability [11]. Furthermore, this is reinforced by the fact that the incorporation of graphene and CNTs in ceramics gives high electrical conductivity and good thermal properties [17,18]. Such composites are very useful in applications that require efficiency in heat dissipation and electrical performance, such as thermal management systems, electronics, and structural parts under high thermal and electrical loads [2].

The potential applications are very wide and diversified for graphene/CNT-reinforced ceramic composites. These composites have found applications in replacing some traditional materials, for instance, gray cast iron within the brake systems in the automotive industry, providing a longer service life and less wear to the surface due to their excellent friction properties [16,19,20]. The application of ceramic technology in tribological phenomena, which encompasses friction, lubrication, and wear, has played an important role in bringing forth efficiency and performance into mechanical systems. In these ways, these materials reduce energy losses and maintenance costs for industrial equipment, which finally makes it reliable and durable.

This review will focus on improving some properties with the incorporation of graphene and CNTs and preparation methods like ball milling and spark plasma sintering to optimize performance. The solution to addressing the limitations of traditional ceramics opened up new opportunities for their application in advanced industries where mechanical, thermal, and electrical reliability are critical.

2. Ceramic Composites

Ceramic composites are a hallmark of material science because they combine the inherent benefits of ceramics with superior mechanical properties obtained through reinforcement. These materials consist of a ceramic matrix combined with reinforcing phases such as fibers [21], particles [22], or whiskers [23], which surpass the traditional brittleness of monolithic ceramics. By virtue of these enhancing features, ceramic composites exhibit increased toughness, strength, and thermal stability and are thus very suitable for many applications in harsh environments in the aerospace [24,25], automotive [26], and biomedical [9,27] industries. Figure 1 summarizes the research progress on ceramic composite materials and their applications.

The primary benefit of ceramic composites is the increase in fracture toughness. In comparison, conventional ceramics are extremely brittle and often fail catastrophically under an applied mechanical loading. However, this problem can be dramatically diminished by introducing these reinforcing materials into a ceramic matrix. Crack deflection, crack bridging, and fiber pull-out are some of the mechanisms explaining the energy dissipation of composites, and thus, their ability to resist fracture. Silicon carbide (SiC) or alumina

(Al_2O_3) fibers, for example, are widely utilized in ceramic composites to enhance the mechanical performance in high-temperature applications [28–30]. In addition to improved toughness, ceramic composites also show superior wear resistance and thermal stability. These properties are a must in most high-performance applications in which materials become exposed to extreme conditions. For example, in aerospace applications, advanced ceramic composites are used in components such as turbine blades and thermal protection systems, which are expected to maintain integrity at elevated temperatures and mechanical stresses [7,24]. At the same time, in the automotive industry, ceramic composites are used for brake discs and other parts that require high wear resistance and thermal conductivity [31]. The principal shortcoming in terms of these applications is the production method for ceramic composites. It is essential to obtain a homogeneous dispersion of reinforcement materials within the ceramic matrix in order to achieve the above-mentioned mechanical properties. Advanced processing techniques are adopted in tailoring the microstructure of ceramic composites to further enhance their overall performance, such as hot pressing [13,29], spark plasma sintering [12,32], and chemical vapor infiltration [33]. They provide better control of the distribution and orientation of the reinforcement; hence, the composites show improved mechanical and thermal properties.

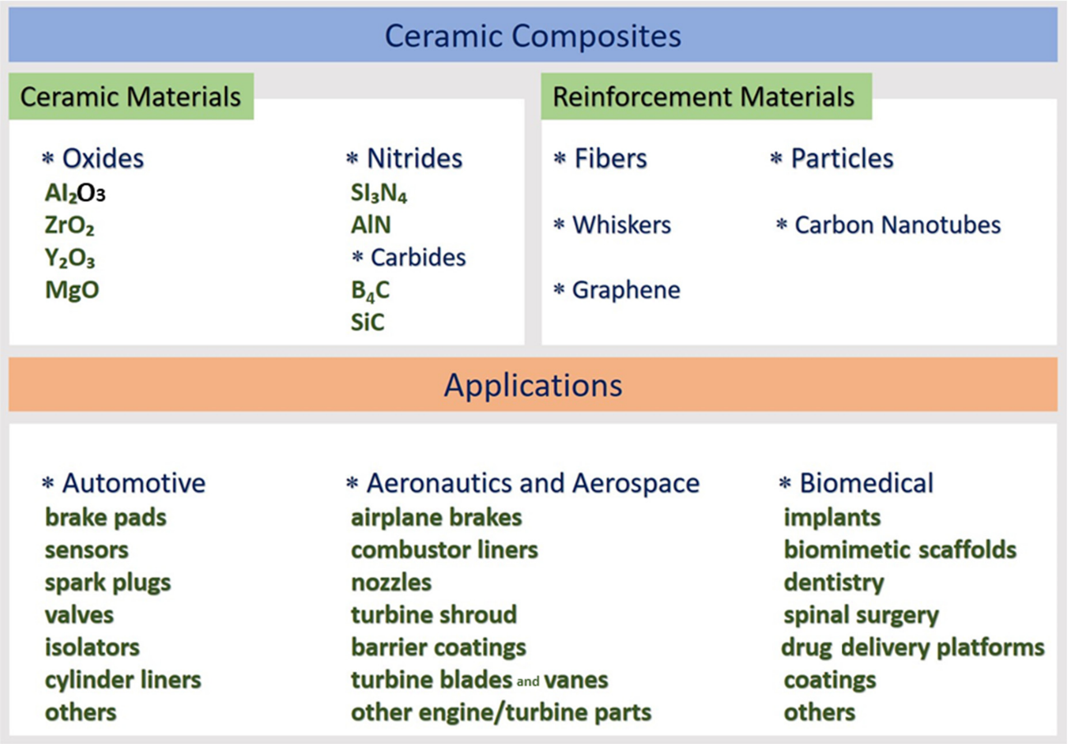

Figure 1. Research progress on ceramic composite materials and their applications.

The present research on ceramic composites looks at the development of hybrid composites by reinforcing them with different combinations to obtain balanced properties. For example, a combination of both CNTs and graphene in the ceramic matrix might strike a balance of properties of strength and toughness with high electrical conductivity. These nanocomposites are being explored for applications in advanced electronics, energy storage devices, and even biomedical implants, where multifunctional properties are required [34–36].

3. Graphene and Carbon Nanotube (CNT)

Graphene is a unique material made of a single layer of carbon atoms set up in a two-dimensional honeycomb design [37]. It was discovered in 2004 and quickly became a focus of study because of its amazing mechanical, electrical, and thermal qualities. As the foundation for graphite, graphene is extremely strong—about 200 times stronger than steel—while still being flexible and super light and thick. This strength, combined with its ability to bend, opens up many possibilities in fields like flexible electronics, structural materials, and advanced composites [38]. One of graphene's best features is its ability to conduct electricity.

It allows electrons to move easily through it with hardly any resistance, making it a great option for upgrading electronic devices [39]. Graphene-based transistors have the potential to be faster and more energy-efficient than other materials like silicon, possibly leading to better and quicker electronics [40]. Its high carrier mobility—which is much better than most other semiconductors—makes it ideal for purposes such as high-frequency electronics, sensors, and super-capacitors [37].

In terms of heat, graphene is considered one of the most promising materials. It has superior thermal conductivity, one of the highest of any known material, making it an excellent heat transfer material [41]. This makes graphene an ideal fit for computer chips, smartphones, and other devices that easily overheat [42]. Graphene's properties can be altered by adding different chemical groups to its surface. Thus, this opens up even more possibilities, like using it in drug delivery systems, sensors for monitoring the environment, and filtration membranes [42–44]. Graphene is truly a game-changing material. Its wide range of features means it can impact industries like electronics, energy storage, and biomedicine in a big way. Carbon nanotubes (CNTs) are cylinder-shaped materials made of carbon atoms arranged in a hexagonal pattern [45]. CNTs exist in three different patterns created by rolling up graphene sheets (hexagonal lattice of carbon atoms) into nanotubes: armchair, zigzag and chiral nanotubes, as explained in Figure 2.

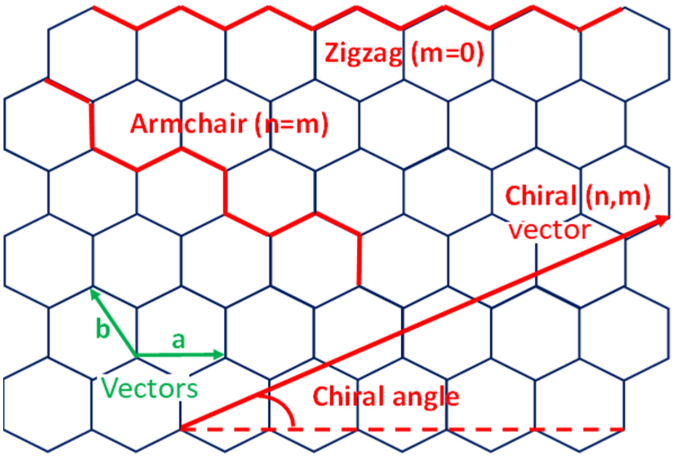

Figure 2. An illustration of how a 2D graphene sheet is rolled to form CNT structures (zigzag, armchair and chiral nanotubes).

CNTs are extremely strong and have special electrical properties, which make them useful in fields like materials science, electronics, and energy [46]. Single-walled carbon nanotubes (SWCNTs) are made of a single layer of carbon atoms rolled into a tube, while multi-walled carbon nanotubes (MWCNTs) have several layers [45]. Because of their small size and ability to conduct electricity, CNTs are ideal for nanoelectronics, drug delivery, and creating strong yet lightweight materials [47].

4. Graphene/CNT Ceramic Composites

Composite reinforcement of graphene and CNTs into ceramic composites is a highly effective strategy in relation to enhancing their properties and performances. These two kinds of nanomaterials possess complementary properties that, when combined, significantly enhance the mechanical and functional properties of the ceramic matrix, thus being suitable for advanced applications in different industries. Table 1 shows a brief summary of the enhanced properties of selected ceramic materials containing graphene and CNT.

The properties of ceramic composites can be significantly enhanced if graphene and CNTs are added to the matrix. Thus, a great number of works have been reported on a ceramic matrix with graphene and CNTs as fillers, which exhibit relevantly different advantages. The benefits of using this material include phenomenal tensile strength, flexibility, and high electrical conductivity, making it a very strong reinforcement material that is capable of stopping the growth of cracks effectively using mechanisms like crack bridging and deflection [18,48]. The effect of the high aspect ratio, together with the superior mechanical properties of CNTs, further enhances these effects because of the even stress distribution within the ceramic matrix, resulting in increased toughness and durability [17]. This dual approach to reinforcement results in a composite material with increased fracture toughness but the value of high strength maintained under a variety of loading conditions [14].

Beyond improving the mechanical properties, the incorporation of graphene and CNTs into ceramics also enhances other functional properties. For example, graphene, together with CNTs, known for their excellent electric conduction and superior thermal conduction, enables the development of ceramic composites that efficiently dissipate heat with enhanced electrical properties [34]. Therefore, graphene- and CNT-reinforced ceramics find particular application in electronic devices, thermal management systems, and structural components exposed to high thermal and electrical loads [39]. Innovative processing techniques have been developed and optimized for these graphene- and CNT-reinforced ceramic composites by utilizing techniques such as spark plasma sintering and chemical vapor deposition [32,49,50].

However, the realization of such promise, which will enable diverse applications of graphene and CNTs in ceramic matrices, is accompanied by several challenges. The dispersions of these nanomaterials should be uniform in the ceramic matrix so as to have consistent properties in the composite. Strong interfacial bonding between the ceramic matrix and the reinforcing agents is essential to fully realize the mechanical and functional benefits of these materials.

Table 1. Properties enhanced by graphene and CNT reinforcements in ceramic composites.

Property	Graphene Reinforcement	CNT Reinforcement	Combined Graphene and CNT Reinforcement
Fracture Toughness	Increased via crack deflection and crack bridging in B_4C [51], Si_3N_4 [52] and Al_2O_3/TiC composite [53]	Improved through crack bridging and pull-out mechanisms in Si_3N_4 [54,55]	Significant enhancement due to synergistic effects in Al_2O_3 [56,57]
Electrical Conductivity	High due to graphene's excellent electron mobility in SiC [58,59]	Moderate; improvement in specific directions depending on CNT alignment Si_3N_4 [54]	Significantly improved with proper dispersion and orientation [60]
Thermal Conductivity	Enhanced by reducing phonon scattering [41,49]	Improved thermal properties due to high aspect ratio and alignment in SiC [61]	Superior performance with proper ratio and dispersion in Al_2O_3 [15,62]
Machinability	Improved due to enhanced toughness and reduced brittleness in Al_2O_3-SiCw ceramic composites [63] and alumina [64]	Increased due to better stress distribution and toughness B_4C [65]	Optimized machinability through balanced reinforcement properties in Al_2O_3 [66]

5. Previous Attempts at Reinforcing Ceramics with Graphene/CNT

Although CNTs and graphene are similar in terms of their chemical bonding consisting of a regular array of benzene rings, they differ in dimensionality and curvature, causing a certain impact on ceramic properties. Thus, in recent years, scientists have attempted to combine the advantages of two-dimensional graphene and one-dimensional CNTs to develop ceramic composites with exceptional properties. One of the most crucial aims of using graphene and CNTs in the reinforcement of ceramics has been to replace the nature of brittleness and low fracture toughness usually associated with traditional ceramics. For example, ceramics such as alumina (Al_2O_3), silicon carbide (SiC) and silica (SiO_2) have been identified with high levels of hardness, thermal stability, and wear resistance [20,67]. Nonetheless, there are limitations to their use in structural applications due to catastrophic failure under stress. By utilizing the remarkable characteristics exhibited by these nanomaterials toward enhancing the overall performance of ceramics, it has been suggested that embedding nanomaterials like CNTs and graphene into these ceramic matrices could be a way out of this problem.

Processing techniques have also been of great interest in the development of graphene/CNT-reinforced ceramics. Spark plasma sintering (SPS) has proved to be an important processing technique in the development of such composites. It enables rapid densification at reduced temperatures and that restricts grain growth, which helps retain the integrity of nanomaterials in the composite during processing [68]. A number of studies, for example, Wang et al. in 2011 [69], Yazdani et al. in 2015 [70] and Shin et al. in 2018 [17], have shown that the SPS method could effectively obtain highly densified Al_2O_3-CNT/graphene composites with great mechanical performance, which means this method may have potential for application in ceramic composite fabrication. Another study by Hou et al. in 2020 showed proper interfacial polarization and better composite performance when using chemical vapor infiltration to distribute CNTs uniformly in a ceramic matrix [50].

Dispersion and bonding are major problems accompanying the development of graphene/CNT ceramic composites due to the limitation in achieving a uniform dispersion of nanomaterials within the ceramic matrix. Agglomerated graphene and CNTs create a weak spot in the composite, thereby reducing its mechanical behavior. Several strategies have been developed to overcome this limitation, among which the preparation of well-dispersed materials by surface functionalization and the use of dispersing agents are the most common. Shu et al. (2019) underlined the key role of strong interfacial bonding between the ceramic matrix and the reinforcing nanomaterials by pointing out how the processing conditions have to be optimized [71].

Electron beam irradiation, on the other hand, has also been studied for its effects on ceramic materials, demonstrating remarkable impacts on their structural and functional properties. Electron beam exposure can significantly influence ceramic and reinforced ceramic properties, with varying outcomes depending on the specific materials (matrix and reinforcement materials) and irradiation conditions. For ceramic matrices, electron beam irradiation can have different effects on various types of ceramics. For example, alumina ceramics alter the grain structure and decrease the surface roughness, with lower electron beam speeds resulting in finer grains [72]. However, the alumina grain size increases after exposure to high speeds owing to the bonding of particles caused by the energy from these electrons. However, phase-reinforced ceramics, for example, the SiC/SiC composite, exhibited evident amorphization and low radioluminescence intensity due to the self-absorption of free carbon after exposure to electron irradiation [73]. In the case of nanomaterial-reinforced ceramics, such as graphene- and CNT-reinforced ceramic composites, irradiation with an electron beam can alter the properties of their composites. For example, electron beam irradiation can be useful for selective modification of graphene layers, which can remove carbon atoms from graphene layers as well as inducing chemical reactions in a controlled manner [74]. Moreover, this could potentially be exploited to fine-tune the interface between graphene and the ceramic matrix, which is important for the overall performance of the ceramic composite. Although electron beam exposure can lead to diverse changes in reinforced ceramics, further research is required to optimize electron beam treatments for various ceramic composites and potential uses.

To conclude, despite extensive studies, research into developing ceramic composites containing CNTs and graphene is continuously conducted using promising techniques. Here, we provide a list of these studies and the key findings and results of each.

5.1. Single-Reinforcement CNTs

By using oxidized Si_3N_4 as a matrix material for single-reinforced ceramic composites containing only CNTs, several physical and mechanical properties, including the density, coefficient of friction, bending strength and hardness, were improved [75]. The ceramic matrix, Si_3N_4, was oxidized for 10 and 20 h at 1000 °C before being milled with sintering additives (4wt.% of Al_2O_3 and 6 wt.% of Y_2O_3) to improve its sinterability in hot isostatic pressing (HIP). Some of the relative improvement in the mechanical properties was attributed to the increase in density caused by oxidative action. Different ceramic materials and different parameters can be used to investigate oxidation effects, and further improvements can be obtained. Similar materials fabricated using HIP were tested for thermal shock resistance and electrical conductivity [54]. The most significant results in terms of thermal shock resistance were obtained when 1 wt.% CNTs were added and 3 wt.% CNTs for the best improvement in terms of electrical conductivity.

A comparative study of the spark plasma sintering (SPS) and hot isostatic pressing (HIP) techniques on CNT/Si_3N_4's properties has been used to compare the results in terms of the microstructure and mechanical properties [76]. Nearly compact composite samples and better mechanical properties were obtained in the case of SPS, as shown in Table 2. However, in a separate study conducted on the same material, more densified samples and higher strength were obtained when higher pressure and a longer holding time were used in the case of HIP [77]. Furthermore, the addition of AlN to the composite could have a positive effect on its mechanical properties and electrical conductivity.

Table 2. Some mechanical properties (density, elastic modulus, shear modulus, hardness, and fracture) of carbon nanotube (CNT)-reinforced silicon nitride composites sintered by SPS (reproduced with permission from [76], Elsevier, 2005).

SPS Samples	Density (g/cm^3)	Elastic Modulus (GPa)	Shear Modulus (GPa)	Hardness (GPa)
4039	3.23	326.21	130.18	20.1 ± 0.9
4040	3.17	285.73	115.10	16.6 ± 0.4
3942	3.24	316.80	124.46	18.3 ± 0.5
4041	3.19	306.16	123.91	19.1 ± 0.6

5.2. Single-Reinforcement Graphene

Graphene, thermally reduced graphite oxide (TRGO) and graphene-coated silicon carbide (GSiC) were employed to reinforce silicon carbide as single-phase reinforcing materials [78]. Pressureless sintering (PLS) was used for fabricating the 2 wt.% graphene-reinforced SiC composite, whereas spark plasma sintering (SPS) produced SiC composites with a higher graphene content of 4 wt.% and 8 wt.%. Graphene/SiC composites with high graphene content, including SP-sintered TRGO and GSiC, have shown a significant improvement in tribological performance.

Hot isostatic pressing (HIP) and spark plasma sintering (SPS) were used to produce Si_3N_4 ceramic composites containing 1 wt.% and 3 wt.% multilayer graphene (MLG) to evaluate their tribological performance [79]. The highest performance was observed when SPS was involved compared to the HIP method, as the results showed that the SPS composites had higher density accompanied by a lower wear rate. Table 3 summarizes the results of the density and wear results.

Table 3. Apparent density and steady-state friction coefficients for the applied wear test conditions of the reference and composite ceramics (Si_3N_4 ceramic composites containing graphene) prepared by different sintering methods (reproduced with permission from [79], Elsevier, 2016).

Sintering Method	MLG (wt.%)	Apparent Density (g/cm^3)	Steady-State Friction Coefficient, μss			
			SiC Ball	Si_3N_4 Ball	SiC Ball	Si_3N_4 Ball
			v = 20 mm/s		v = 200 mm/s	
HIP	0	3.23	0.385	0.679	0.498	0.597
	1	3.27	0.396	0.680	0.501	0.639
	3	2.80	0.445	0.704	0.550	0.803
SPS	0	3.23	0.348	0.769	0.712	0.671
	1	3.29	0.363	0.683	0.448	0.716
	3	3.11	0.375	0.735	0.473	0.684

5.3. Dual (Hybrid)-Reinforcement Graphene/CNTs

The pioneering studies laid the foundations for showing the potential of CNTs as a reinforcing phase in ceramics. Shah et al., in 2021, studied the effect of adding graphene and CNTs to Al_2O_3 ceramic as reinforcements and proved that it remarkably increases the fracture toughness and bending strength of the composites [15]. In a similar way, Rahman et al. proved back in 2018 through their study that graphene and CNTs are an ideal form of reinforcement in order to increase the mechanical properties of alumina ceramics, thus proving the potential in being a reinforcement material for graphene and CNT [57]. However, while the addition of CNTs and graphene to alumina appears to consistently enhance the fracture toughness, their effects on the microhardness are variable or ineffective. They attribute this behavior to CNTs, which act as lubricants during indentation, accelerating the grain slippage despite higher densification and lower grain growth. Figure 3 displays the densification of alumina ceramic particles using SEM images (a–c) and the hardness and fracture toughness results (d,e). These works were performed in greater detail, focusing on understanding the mechanisms of reinforcement by graphene and CNTs. Similar results have been shown in previous works by Yazdani et al. in 2015 [70,80], Mukherjee et al. in 2017 [81] and Sharma et al. in 2019 [20] on improving the mechanical properties of alumina.

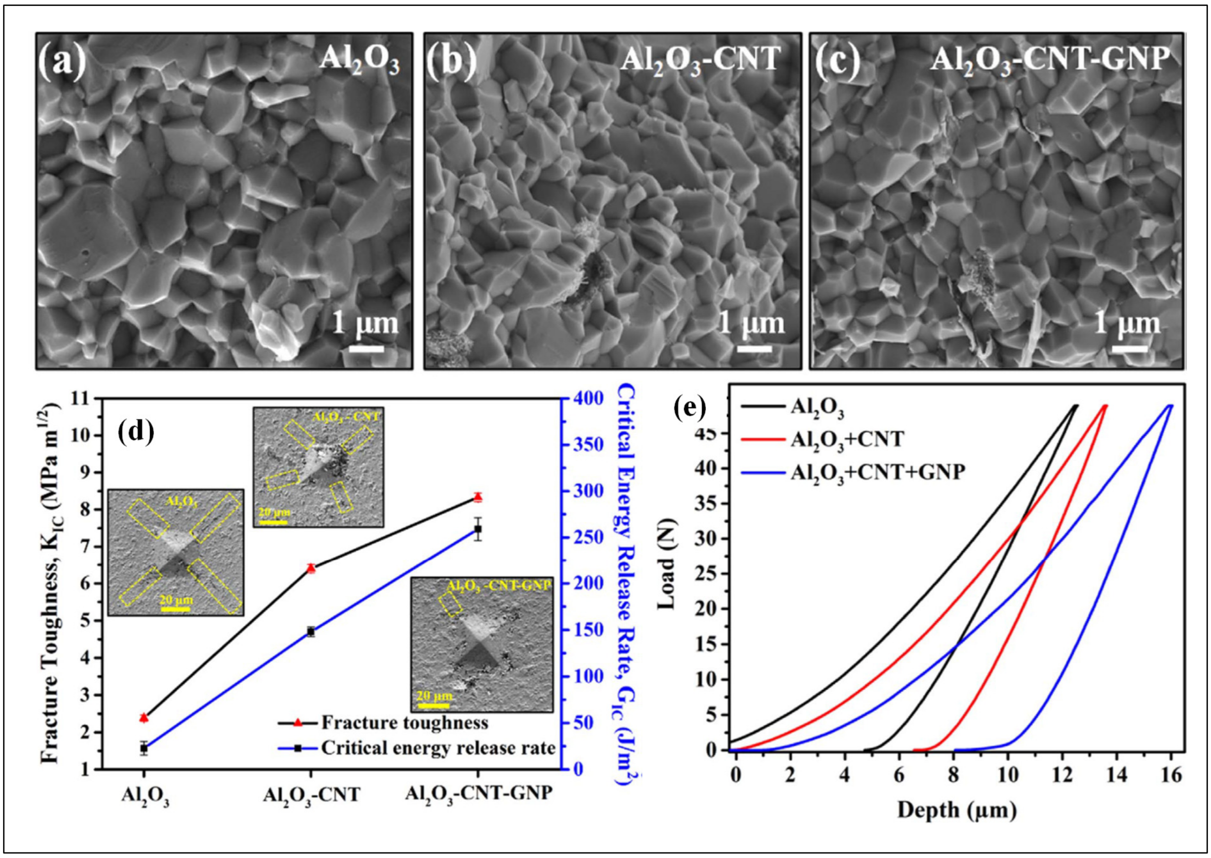

Figure 3. SEM images of Al_2O_3 composite fracture surfaces reinforced with CNTs and graphene (GNP), showing the reduction in the grain size of Al_2O_3 (**a**–**c**) and increasing the fracture toughness, together with reducing the hardness of the Al_2O_3 composite (**d**,**e**), respectively. Adapted with permission from [57], Elsevier, 2018.

Xu et al. [82] and Sun et al. [83] demonstrated that CNT/graphene was effective in crack bridging and pull-out mechanisms in SiC ceramics, yielding composites with improved toughness. Similar studies have demonstrated similar behavior in other ceramic materials, for example, TiO_2-MgO ceramic by Rouway et al. in 2020 [18], Al_2O_3-TiC ceramic composites by Sun et al. in 2020 [68], Cu/Ti_3SiC_2/C nanocomposite by Jiang et al. in 2017 [84] and Si_3N_4 by Tapasztó et al. in 2011 [85]. Graphene and CNTs can also be incorporated to enhance functional properties rather than being solely used for mechanical reinforcement. In another study on ultra-high-temperature ceramic (UHTC) by Rouway (2020), with the addition of graphene and CNTs, the material finds its application in aerospace and electronics composites due to its performance in terms of thermal conductivity and electricity [18].

The hybrid reinforcement of ceramic composites (Si_3N_4) containing graphene and CNTs provides a combined effect on their morphological and mechanical properties. Dispersion of these materials within ceramic matrices is a key factor in achieving the maximum use of these materials. Thus, in a previous study, Si_3N_4 composites showed better dispersion in Si_3N_4 containing graphene than those with CNTs [85]. These composites exhibited mechanical properties improved by 10–50% compared with composites containing CNTs, which were prepared under the same parameters. Motivated by this idea, we continue to explore the advantages of hybrid reinforcements with ceramic matrices for better performance.

6. The Main Parameters Influencing CNT/Graphene Ceramic Reinforcement

6.1. Optimal Ratio of Graphene to CNTs in Ceramic Matrices

The ratio of graphene to CNTs is crucial in shaping the final properties of ceramic composites. Different uses might need specific compositions to hit the right performance marks. For instance, alumina (Al_2O_3) ceramics show a big boost in mechanical strength with 1 wt.% CNT and 0.5 wt.% graphene content consolidated by hot press (Yazdani et al. in 2014) [86] or SPS (Rahman et al. in 2017) [57]. This boost happened because these nanomaterials were uniformly distributed and worked together to strengthen the ceramic matrix by bridging cracks and stopping them from spreading. Figure 4 demonstrates the toughening mechanism of CNT bridging using high-magnification TEM images of the fracture surfaces of Al_2O_3-graphene and -CNT composites. On the other hand, based on a study conducted by Yazdani et al. in 2015, adding just 0.5 wt.% CNT and 0.5 wt.% graphene content to ceramics synthesized by SPS can significantly enhance their mechanical properties, showing that even a small amount of these nanomaterials can make a big difference [70].

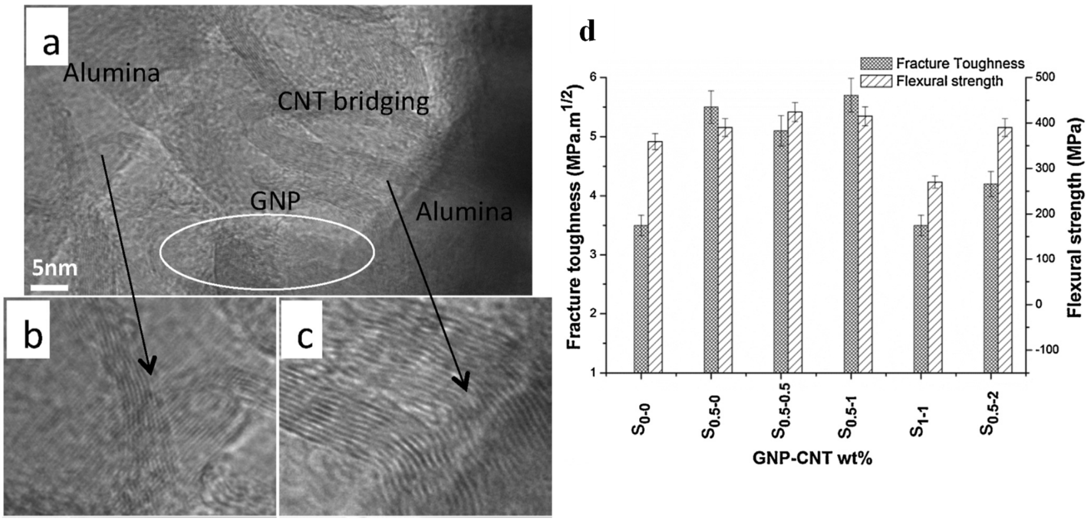

Figure 4. The toughening mechanism of CNT bridging using high-magnification TEM images on the fracture surfaces of the Al_2O_3-graphene (GNP) and -CNT composite (**a**–**c**) and the fracture toughness and flexural strength of the Al_2O_3 composite at different graphene and CNT ratios (**d**). Adapted with permission from [86], Elsevier, 2015.

For aluminum oxide/titanium carbide (Al_2O_3/TiC) composites, research led by Daming Sun in 2020 found that the most effective results came from a mix of 0.8 wt.% multi-walled carbon nanotubes and 0.2 wt.% graphene fabricated by SPS [68]. Crack deflection, bridging, and branching of graphene and CNTs were observed as the toughening mechanisms of Al_2O_3/TiC composites reinforced with graphene and CNTs. Regarding thermal conductivity, monolithic alumina ceramics perform superiorly with low concentrations of graphene and CNTs—specifically, 0.4 wt.% graphene and 1 wt.% CNTs compared to other reinforcement contents [15]. This small amount effectively reduces the phonon scattering, improving the thermal conductivity without compromising the ceramic's structural integrity.

The way these two nanomaterials work together makes the composite not only stronger but also better at conducting electricity. This means it is ideal for high-tech applications where both strength and conductivity are important. Also, it makes the composite lighter, which helps save costs and improves efficiency. These properties make this material a strong choice for modern engineering uses, from fuel cells to other electronics. The balance of toughness and performance provided by this composite makes it a leading candidate for cutting-edge engineering solutions.

6.2. *Dispersion and Distribution*

It is important to ensure that graphene particles and CNTs are uniformly distributed throughout a ceramic matrix in order to maximize the performance of composite materials. The distribution of these nanomaterials has a direct impact on improving the mechanical, thermal, and electrical properties of the composite. However, because graphene and CNTs naturally agglomerate, especially at higher concentrations, achieving this uniformity is a significant challenge.

The strong van der Waals forces between graphene and CNTs, which promote cluster formation rather than a homogeneous dispersion, are the main cause of this agglomeration [48]. In addition to introducing possible weaknesses within the ceramic matrix that could serve as sites for crack initiation, this clustering lowers the effective surface area available for reinforcement and ultimately compromises the mechanical strength of the composite.

To address these issues, hot pressing (HP) and spark plasma sintering (SPS) are some of the advanced processing techniques [68,70,86]. This is effective in promoting a uniform distribution of the reinforcing nanomaterials and guaranteeing strong interfacial bonding between ceramics and graphene/CNTs. For example, the fracture surface of Al_2O_3-TiC ceramic reinforced with graphene and CNTs at different contents showed that graphene particles were embedded in the Al_2O_3 grain boundaries, according to a study by Sun et al. (2020) (Figure 5). The SEM of the fracture surfaces of these composites exhibited a rough surface that showed several broken particles. Also, no plastic deformation, or only rarely, was observed at the fracture surface, which indicated the brittleness of the materials. Figure 5b indicates, in the red circled area, that graphene could form bridges at the crack ends. Additionally, the study shows in Figure 5d–f that the CNTs were agglomerated at the grain boundaries in the case of a high CNT content, leaving the grains to be gradually refined, resulting in improving the mechanical properties [68]. In addition to enhancing the mechanical properties, these methods serve to maintain the inherent advantages associated with nanomaterials, including electrical and thermal conductivity [15]

Despite their effectiveness, advanced methods like hot pressing and spark plasma sintering (SPS) still have challenges, like selecting proper dispersing agents for graphene and CNTs to avoid agglomeration. On the other hand, the optimal amount of graphene and/or CNTs can be crucial in enhancing the strength, toughness and other properties without scarifying other properties like hardness [57]. Another promising idea is using functionalization to change the surface of graphene and CNTs to make them better suited to the ceramic matrix. This can improve the bonding, lowering the agglomeration and making the reinforcement more effective [36]. While functionalization has shown encouraging results, more research is needed to enhance nanomaterials' beneficial features while maintaining their overall performance.

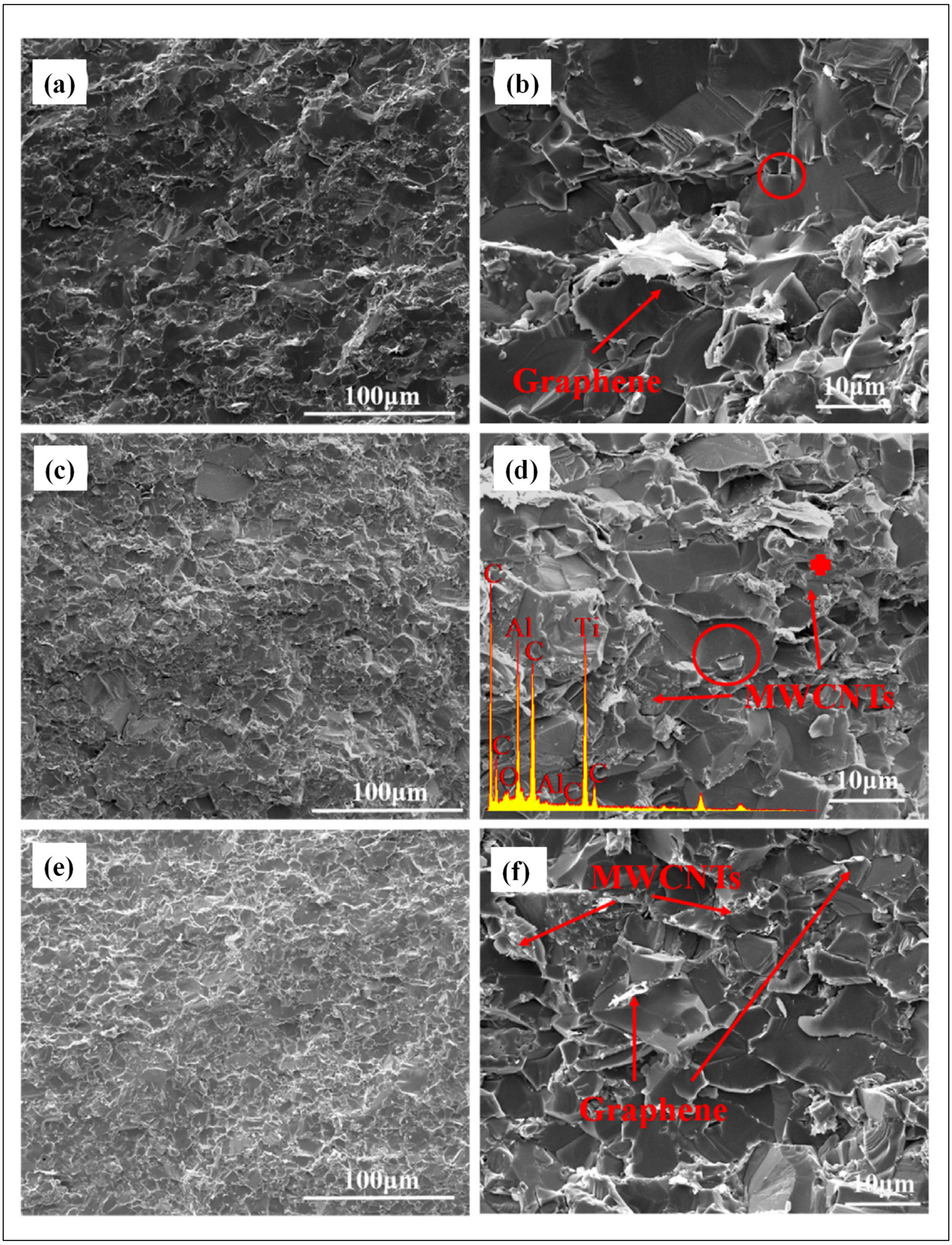

Figure 5. SEM and EDS profiles of the fracture of Graphene/CNT-reinforced Al_2O_3-TiC ceramic composite with the following contents: (**a**,**b**) 0.5 wt.% MWCNTs/0.5 wt.% Graphenes; (**c**,**d**) 0.7 wt.% MWCNTs/0.3 wt.% Graphenes and (**e**,**f**) 0.8 wt.% MWCNTs/0.2 wt.% Graphenes. Reproduced with permission from [68], Elsevier, 2020.

6.3. Effects of Graphene Grain Sizes and Carbon Nanotube Sizes

One critical factor that affects the performance of ceramic composites is the size of the graphene and CNTs, owing to the remarkable impact of these nanomaterials on the behavior of ceramic products. Studies have shown their influence on several properties, including the interfacial characteristics, microstructures and functional properties of ceramic composites.

For example, Shahedi Asl et al. in (2016) investigated the effect of MWCNTs on the densification process and mechanical properties of ZrB_2-SiC ceramic composites [87]. The results showed that the incorporation of CNTs inhibited grain growth in composites, thus improving their fracture toughness significantly via crack bridging and pull-out detection methods. However, CNTs reduced the hardness slightly due to their lubrication action [87]. The size of graphene has a crucial influence on the interfacial characteristics, microstructures and mechanical properties of ceramic composites. Ahmad et al., in 2016, reported that adding graphene with silicon carbide nanoparticles leads to a significant decrease in the grain size of alumina ceramics from 1500 nm to 300 nm. This reduction in grain size resulted in increased toughness and hardness, indicating that smaller particle sizes improve the mechanical strength of ceramic composites, which is explained in Figure 6 [88]. The work of Wu et al. (2021) focused on how the size and amount of graphene affect the grain change in composites of an aluminum matrix reinforced with graphene. It was discovered from this study that smaller sizes of graphene had better mixing with the matrix, hence improving its ability to pin grain boundaries, which leads to finer grains. The enhanced mechanical properties exhibited by these materials, such as higher strength and better load transition capabilities, were due to their improved microstructure [89]. In addition to the significant influence of the graphene sizes on the interfacial characteristics, microstructures and mechanical properties, they also impact the interfacial chemistry reaction products and sizes of ceramic products, based on study by Wang et al. [90]. The results demonstrated that the interfacial reaction products between graphene and Al_2O_3 changed from Al_4O_4C to Al_4C_3 and the sizes of products were increased with the increase in graphene thickness [90].

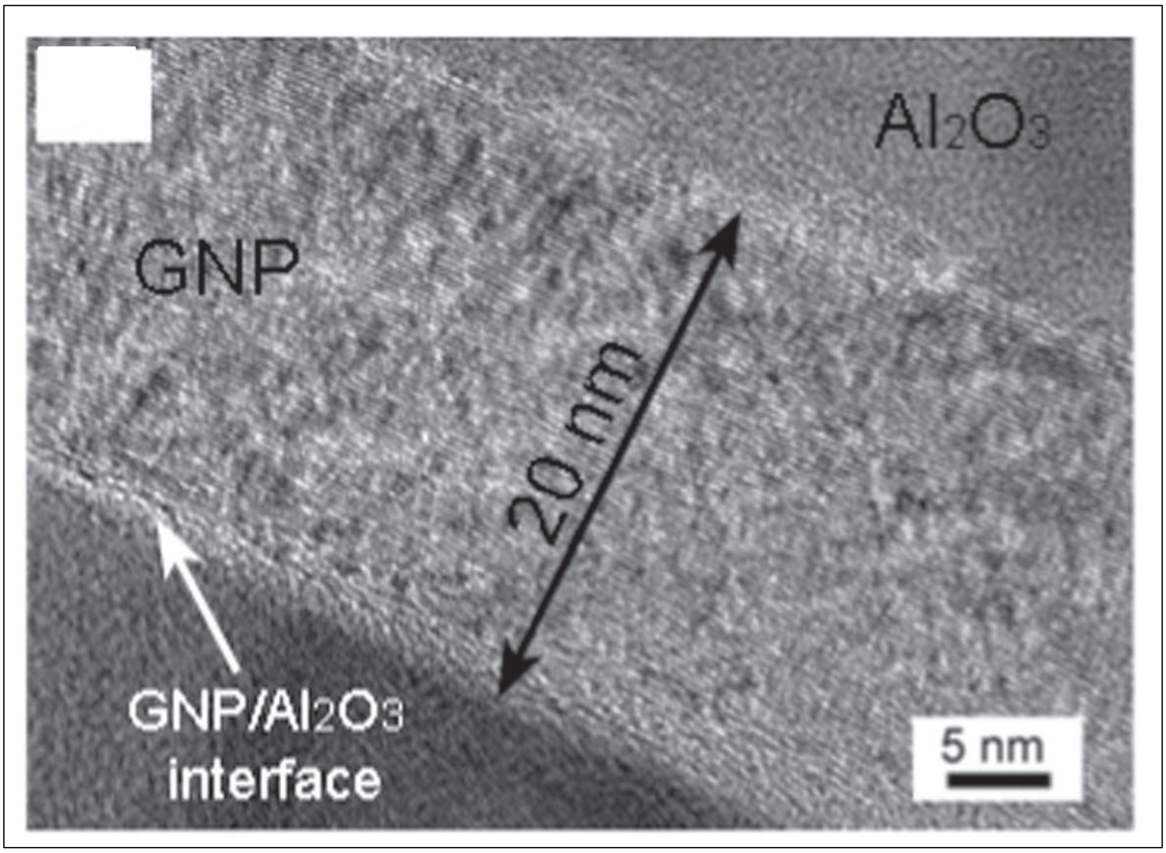

Figure 6. TEM images of the Graphenes/Al_2O_3 interface. The interface between the outer graphene (GNP) layer and the ceramic matrix may have hindered the crack propagation. Reproduced with permission from [88], IOP Publishing, 1990.

7. Fabrication of Graphene/CNT Ceramic Composites

7.1. Ball Milling

Ball milling, initially created for powder metallurgy, is an essential method for ensuring the uniform and homogeneous dispersion of advanced ceramic powders and their composites. This method involves using high-energy collisions between balls and the walls of a rotating jar to achieve fine particle sizes and uniform distributions. The ball-milling process is essential for preventing particle agglomeration and ensuring the homogeneous dispersion of CNTs in structural ceramic matrices. These factors are critical as they significantly influence the final composite's properties, including the strength, density, wear resistance, and friction [2].

The simplicity and energy efficiency of ball milling make it a popular choice for synthesizing ceramic/CNT powder mixes. This method promotes high grain refinement and phase homogenization, which are vital for the performance of the final product. The high milling energies generated during ball milling break the interlayer Van der Waals forces between carbon surfaces, reducing the agglomeration of CNTs and ensuring their high surface energy is maintained. The high rotational speed of the ball-milling devices causes the balls to strike the jar walls with significant force, facilitating high-energy collisions that contribute to effective particle size reduction and mixing [91]. Table 4 displays the effect of the ball-milling time on the size of the powder particles and the specific surface area of the SiC powder. If the ball-milling time increased, the powder particles size decreased. Additionally, the oxygen content and mass loss of SiC balls gradually increased [92]. This process is followed by sintering, which consolidates the powder mixture into a solid form, completing the creation of an advanced ceramic composite with improved mechanical and functional properties [93].

Table 4. Characterizations of ball-milled SiC powder. Reproduced with permission from [92], Elsevier, 2021.

Materials	Particle Size (μm)	Specific Surface Area (m^2/g)	Oxygen Content (wt.%)	Wastage of SiC Balls (wt.%)	SiC Calculated [a] Content (wt.%)	SiC Content (wt.%)	Theoretical Density (g/cm^3)
B0	6	1.95	1.06	0	0	0	4.52
B6	2.86	3.60	2.15	1	3.81	4.76	4.43
B12	1.96	4.98	2.81	1.65	7.05	7.62	4.38
B18	1.62	5.68	3.45	2.25	9.34	10.11	4.34
B24	1.34	6.15	4.02	2.75	10.86	12.09	4.31

[a]: SiC contents were obtained via XRD data. B0, B6, B12, B18, and B24: ball-milling time (0, 6, 12, 18, 24 h).

7.2. Spark Plasma Sintering Method

Spark plasma sintering (SPS) is a widely used powder metallurgy process that enables the rapid synthesis of a broad range of advanced materials with fine grain sizes at relatively low temperatures. SPS is particularly effective for fabricating ceramics and ceramic composites. During the SPS process, the mixed powder of CNTs and graphene and ceramic is sintered under the combined effect of a pulsed direct current (PDC) and applied pressure within a vacuum chamber. The powder is placed in a die and then pellet-pressed by a plunger, while a DC current is passed through the die and the sample. The heating rate, applied pressure, and current are the three main parameters that determine the microstructural and mechanical properties of the sintered pellet [94,95]. The mechanisms and advantages of SPS are well documented. Guillon et al. (2014) highlighted that SPS combines rapid heating with applied pressure, leading to efficient densification and minimal grain growth. This is crucial for maintaining the fine microstructure of nanomaterials, which directly correlates with improved mechanical properties such as hardness and toughness [96]. The process involves passing a pulsed direct current through a graphite die containing the powder mixture, which generates heat internally and uniformly across the sample. This method reduces the likelihood of thermal gradients and enhances the homogeneity of the sintered material.

SPS offers several advantages over traditional sintering methods such as hot pressing and hot isostatic pressing (HIP). It allows the consolidation of high-temperature ceramics, metals, and composites within a few minutes, with heating rates up to 100 °C per minute [13]. This rapid processing significantly reduces the duration and energy costs while maintaining high thermal efficiency due to the absence of external heating elements. The SPS process heats the sample by passing a highly pulsed direct current through a graphite die and the sample itself. This method ensures uniform heating and minimizes grain growth, resulting in materials with superior mechanical properties and finer microstructures compared to those produced by conventional methods.

Despite its advantages, SPS also presents certain challenges. Suarez et al. (2013) discussed the difficulties associated with controlling the microstructure and properties of the final product due to the rapid heating and cooling rates. Moreover, the need for graphite dies can introduce carbon contamination, which must be carefully managed depending on the material system [97]. The ability to produce materials with tailored properties makes SPS an invaluable tool in material science and engineering. As research progresses, further developments in SPS technology and techniques are expected to overcome the existing challenges and broaden the scope of its applications.

The applications of SPS are vast, ranging from structural ceramics used in aerospace and automotive industries to functional materials for electronic and biomedical devices. SPS represents a powerful sintering method that combines efficiency, precision, and versatility, making it ideal for producing high-performance ceramic composites. Its ability to maintain fine microstructures and enhance material properties positions SPS as a critical technology for future advancements in various high-tech industries.

7.3. Hot-Pressing Method

Hot pressing is a conventional sintering method that combines high pressure and high temperature to compact and sinter powder materials. This technique, also known as pressure-assisted sintering, involves applying pressure to the powder of graphene/CNT-reinforced ceramic composites to form dense pellets or films. The simultaneous application of high pressure and temperature enhances the density of the composites by improving the bonding between the ceramic matrix and the reinforced graphene and CNTs. This leads to significant improvements in the mechanical properties of the composites [71]. For instance, mullite/CNTs-based composites fabricated using the hot press method at 1600 °C exhibited a 10% increase in bend strength and a 78% enhancement in fracture toughness compared to monolithic mullite. This improvement is attributed to the efficient load transfer and crack-bridging mechanisms facilitated by the well-dispersed CNTs within the ceramic matrix [98]. The hot press technique is advantageous because it allows for the production of dense, high-strength composites with superior mechanical properties. The combination of high pressure and temperature results in enhanced interfacial bonding and reduced porosity, which are critical for the performance of CNT/ceramic composites in various high-stress applications [99]. The differences in the wear coefficients for the Si_3N_4/MLG composite and SiC between the two techniques (HIP and SPS) are represented in Figure 7 [79].

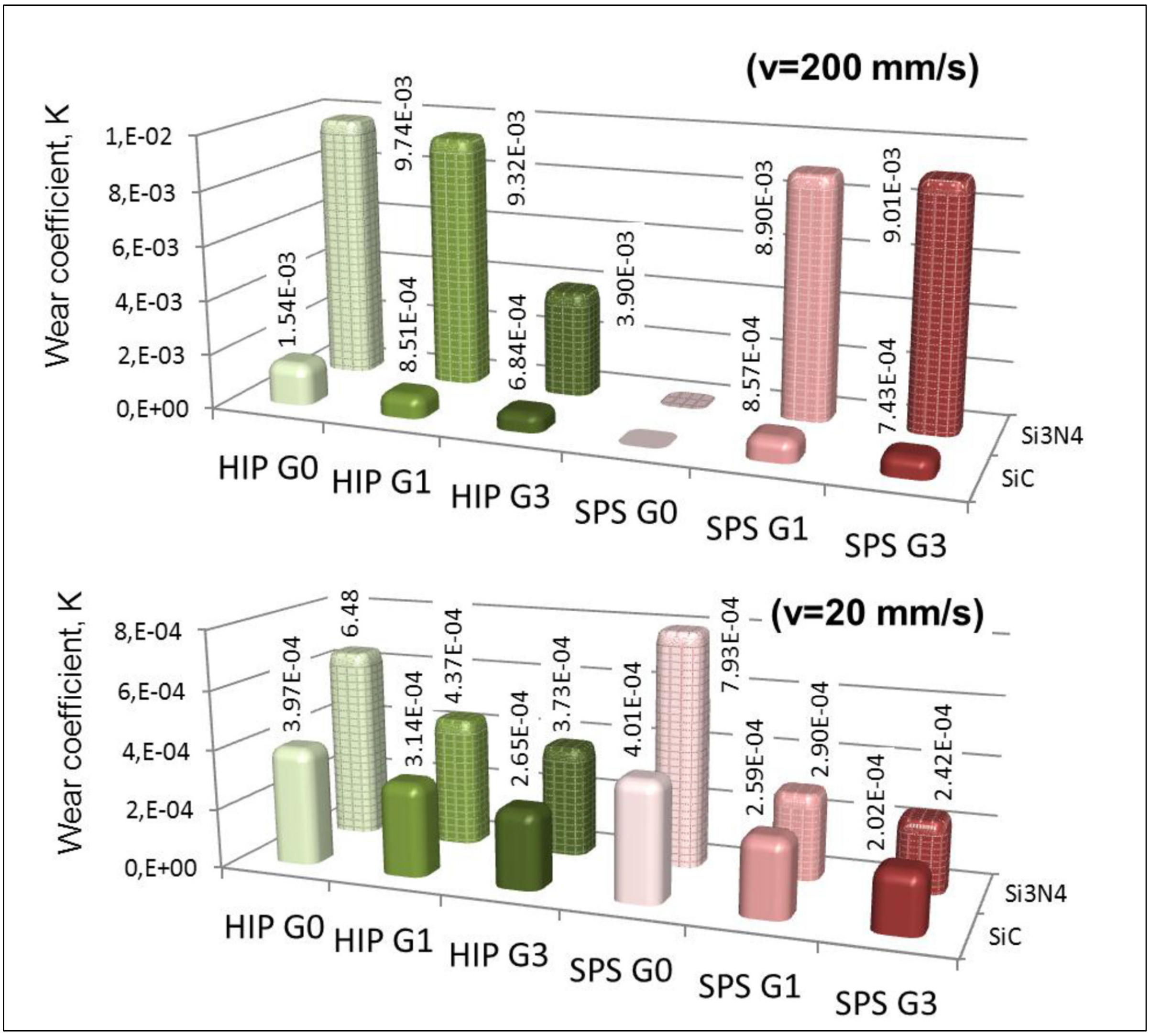

Figure 7. Comparison of the wear coefficients for Si_3N_4 ceramic reinforced by MLG and SiC ceramic fabricated by HIP and SPS (v = 20 and 200 mm/s sliding speeds). Reproduced with permission from [79], Elsevier, 2016.

8. Machine Learning for Ceramic Composites

Machine learning (ML) has grown in prominence due to its scope as a powerful tool for processing vast amounts of data and predicting material properties based on such information. During the past decade, with the fast progress in artificial intelligence, many fundamental properties of materials can now be computed using simulations, with considerable accuracy. This has enabled researchers to explore and understand materials' characteristics faster than traditional methods. Thus, methods such as this method, the ML method, can be applied to simulate a wide range of mechanical, thermal and electrical behaviors of materials like ceramic composites at the nano- and continuum-scale. Therefore, ML can be used to optimize ceramics' performance, providing guidance for future applications. ML can also be used to develop more reliable and accurate ceramic behavior models. For example, Qadir et al. in 2024 applied machine ML using extreme gradient boosting to predict the hardness of graphene-based Si_3N_4 [100]. They developed a model, based on data sourced from the literature, focused on parameters that have a substantial influence on the hardness of graphene-reinforced ceramic materials. These parameters include the graphene content and type, starting materials, and density and ratio of α and β phases, in addition to sintering parameters such as the holding time, sintering pressure and sintering temperature. They concluded that the graphene content, density, and factors affecting the densification process play a key role in achieving high-hardness Si_3N_4 ceramics, as shown in Figure 8 [100].

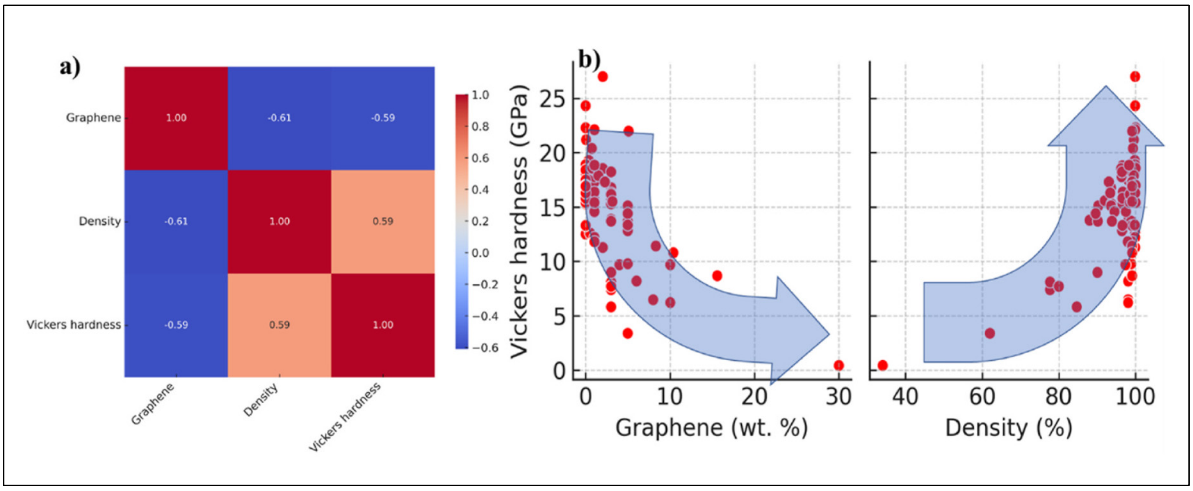

Figure 8. Illustrates the correlation and trends between the graphene content, density, and Vickers hardness of composites: (**a**,**b**) show that the Vickers hardness decreases with increasing graphene content, while it increases with increasing density [100]. Reproduced from [100], Elsevier, 2024.

Oey et al. conducted a study on ML to estimate the compressive strength of concrete from knowledge of its mixture proportions [101]. According to their findings, the ML estimation errors are typically similar to the measurement repeatability of the relevant American Society for Testing and Materials (ASTM) test methods. In this way, they consider the influence of the binder composition and fineness [101]. A study performed by Lehnert et al. applied ML to quantify the microstructural composition of C/C–SiC based on the process parameters and raw materials selection based on data from 123 samples of C/C–SiC [102]. Based on their findings, the most critical factors for receiving either high or low amounts of single-fiber siliconization density in the siliconized state are the open porosity and mass [102]. Thus, in brief conclusion, these studies as well as others [103,104] have shown that ML is an effective tool to predict the most critical properties of materials, including ceramic materials, with high accuracy, to tailor materials and their properties for specific applications.

9. Conclusions

This review demonstrates how far we have come in reinforcing ceramics with graphene and carbon nanotubes (CNTs), highlighting their drastic effects on the mechanical, thermal, and electrical characteristics of ceramic composites. The method of incorporating graphene and CNTs into ceramic matrices has been shown to be very useful in solving the problem of the brittle nature that is common to ceramics; hence, widening their scope in high-performance sectors such as aerospace, automobile industry, and biomedicine.

The fracture toughness, machinability, and thermal stability are significantly enhanced in ceramic matrices by the incorporation of graphene and CNTs. The unique mechanical properties of these nanomaterials, such as the high tensile strength, flexibility (in the case of graphene), and high aspect ratio (in the case of CNTs), largely contribute to the effective stress distribution and crack arrest mechanisms. These improvements allow ceramic composites to maintain high strength under a variety of loading conditions, making them suitable for demanding applications.

Through this review, it becomes evident that optimizing the ratios, sizes, and distributions of graphene and CNTs in ceramic matrices is critical for achieving optimal performance outcomes. Minor additions of these nanomaterials consistently resulted in drastically enhanced electrical and thermal conductivity, especially when they were evenly distributed throughout the matrix. Such uniformity in dispersion and strong interfacial bonding can only be accomplished via advanced processing methods like spark plasma sintering (SPS) as well as hot pressing (HP). This enables composites to keep their original benefits from the various nanomaterials used. Even though reinforced ceramics offer exceptional properties, ongoing challenges, particularly those related to brittleness, reinforcement distribution, and interfacial characteristics, remain critical to their widespread use. Addressing these issues using innovative manufacturing techniques and carefully controlling interfacial properties, as well as the use of optimal ratios of reinforcements and processing parameters, which are highlighted in this review, could lead to significant advancements in the field of reinforced ceramics. Furthermore, overcoming these challenges is vital for realizing the mechanical and functional benefits of graphene- and CNT-reinforced ceramics. Thus, future research should continue to explore innovative processing methods and surface functionalization techniques to overcome these obstacles and further enhance the performance of ceramic composites.

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