

Review Article

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Research on the interface properties and strengthening–toughening mechanism of nanocarbon-toughened ceramic matrix composites

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Abstract: Nanocarbon materials (carbon nanotubes, graphene, graphene oxide, reduced graphene oxide, etc.) are considered the ideal toughening phase of ceramic matrix composites because of their unique structures and excellent properties. The strengthening and toughening effect of nanocarbon is attributed to several factors, such as their dispersibility in the matrix, interfacial bonding state with the matrix, and structural alteration. In this paper, the development state of nanocarbon-toughened ceramic matrix composites is reviewed based on the preparation methods and basic properties of nanocarbon-reinforced ceramic matrix composites. The assessment is implemented in terms of the influence of the interface bonding condition on the basic properties of ceramic matrix composites and the methods used to improve the interface bonding. Furthermore, the strengthening and toughening mechanisms of nanocarbon-toughened ceramic matrix composites are considered. Moreover, the key problems and perspectives of research work relating to nanocarbon-toughened ceramic matrix composites are highlighted.

Keywords: ceramic matrix composites; interface properties; strengthening and toughening mechanisms; nanocarbon materials; nanocarbon dispersion

1 Introduction

Ceramic materials possess high hardness, stability and strength; however, their low fracture toughness and brittleness limit their applications [1]. Different from metal materials, ceramic materials have no capability to slip and produce plastic deformation at room temperature, and they are susceptible to cracks, impurities, pores, and other defects that render them brittle [2–5]. Nanocarbon materials (carbon nanotubes, graphene, graphene oxide, reduced graphene oxide, etc.) have excellent thermal, electrical, and mechanical properties. Extensive research has shown that nanocarbon can enhance many properties of ceramics, for example, the mechanical, frictional [6–9], electrical [10–13], and thermal properties [14–16]. As a result, nanocarbon is regarded as an ideal reinforcing phase in ceramic matrix materials. In particular, the composites in these studies exhibit outstanding improvement of the mechanical properties that results from the strengthening and toughening effect of nanocarbon. In recent years, nanocarbon materials used to reinforce polymer composites has also attracted wide attention [17–21]. However, the application of nanocarbon faces some great challenges, as follows. (I) Nanocarbon is difficult to disperse in ceramic matrix composites because of its considerably large specific surface area, surface energy, van der Waals forces caused by the intermolecular electrical dipole moment, and interactions between functional groups, along with easy aggregation and entanglement properties [22]. (II) The interface invasion between nanocarbon and ceramic are deemed unsuitable because they differ in surface tension and density. In addition, during sintering, the temperature is hard to determine. Interface bonding is reduced at high temperatures, as nanocarbon may be damaged. (III) There is no uniform method to measure ceramic matrix composites with nanocarbon. Because a rigorous toughness should be measured from the energy releasing rate, *i.e.*, the energy needs to make the crack propagating

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Table 1: The common methods of toughness measurement

Authors	Materials	Sintering	Toughness (Mpa·m ^{1/2})	Methods	Improvement
Zeng <i>et al.</i> [88]	0.09wt%GO/ZrO ₂	SPS	10.64	Anstis formula	175%
Ramirez <i>et al.</i> [70]	4.3vol%rGO/Si ₃ N ₄	SPS	10.4	Surface crack in flexure method (SCF)	135%
Liu <i>et al.</i> [29]	1.5vol%rGO/B ₄ C	HPHTS	8.76	Depth-sensing Indentation	131%
Saheb <i>et al.</i> [3]	1wt%CNT/5wt%SiC/Al ₂ O ₃	SPS	7.1	Direct crack measurement (DCM)	97%
Ahmad <i>et al.</i> [45]	4vol%CNT/Al ₂ O ₃	HPS	6.47	Single-edge notched beam (SENB)	96%
Bocanegra-Bernal <i>et al.</i> [23]	0.1wt%MWCNT-CIMAV/Al ₂ O ₃	HIP	3.9	Indentation fracture	63%
Yazdani <i>et al.</i> [121]	0.5wt%GNPs/1wt%CNT/Al ₂ O ₃	HPS	5.7	Single-edge notched beam (SENB)	63%
Ahmad <i>et al.</i> [2]	0.75wt%GNPs/Al ₂ O ₃	HF-IH	7.79	Direct crack measurement (DCM)	45%
Zhang <i>et al.</i> [25]	1wt%graphene/Si ₃ N ₄	HPS	8.7	Vickers indentation method	38%
Tonello <i>et al.</i> [102]	4vol%GNP/SiC	Pressureless sintered	6.6	Pre-cracked beam	34%
Zhang <i>et al.</i> [114]	1wt%GPLs/TiC/Si ₃ N ₄	HPS	9.6	Single-edge notched beam	33%
Sedlák <i>et al.</i> [111]	6wt%GPLs/SiC	HP	4.4	Direct crack measurement (DCM)	30%
Shin <i>et al.</i> [90]	1wt%rGO/Al ₂ O ₃	SPS	4.7	Crack length measurement	27%
Liu <i>et al.</i> [106]	3.0vol%GNS/TiC	SPS	4	Vickers indentation method	26%
Shin <i>et al.</i> [90]	1wt%SWCNT/Al ₂ O ₃	SPS	4.2	Crack length measurement	14%
Bocanegra-Bernal <i>et al.</i> [4]	0.1wt%SWCNT/Al ₂ O ₃	PLS	3.3	Indentation fracture	14%
Bocanegra-Bernal <i>et al.</i> [4]	0.1wt%MWCNT/Al ₂ O ₃	Sinter+HIP	3.3	Indentation fracture	10%

to a per unit length. However, the composites are severe anisotropic. Therefore, for the composites people just use energy dissipation (*i.e.*, the integral of stress-strain curves) to define the toughness. The common methods used for the evaluation of the resulting composite materials have been tabulated (see Table 1) [23–30]. The foregoing are critical factors that affect the properties of nanocarbon-strengthened and-toughened ceramic matrix composites.

In this paper, the fabrication, basic properties, interfacial properties, and strengthening–toughening mechanism of nanocarbon-toughened ceramic matrix composites are briefly reviewed. Based on the perspective of the nanocarbon interface state and the interface bonding strength of nanocarbon-toughened ceramic matrix composite materials, this paper gives some suggestion for future research works about the problem of dispersion and interface in the section 2 and 3, but about measuring method, there is a lack of literature to discuss.

2 Nanocarbon dispersion in ceramics

As mentioned above, nanocarbon has a tendency to spontaneously condense, and although it is beneficial in promoting the formation of functional networks, the aforementioned disadvantages interfere in the preparation of nanocarbon-reinforced ceramic matrix composites [26]. More specifically, aggregated nanocarbon causes stress concentrations and even acts as a structural defect to reduce the mechanical properties of nanocarbon-reinforced ceramic matrix composites [24, 31]. In addition, apart from the grain size, reinforcing phase, and interfacial strength, dispersion is one of the most critical factors that affects the mechanical properties of nanocarbon-reinforced ceramic matrix composites [32, 33]. Therefore, favourable nanocarbon dispersion in the ceramic matrix is fundamental to obtaining excellent mechanical properties. Although nanocarbons with good dispersion can be obtained by

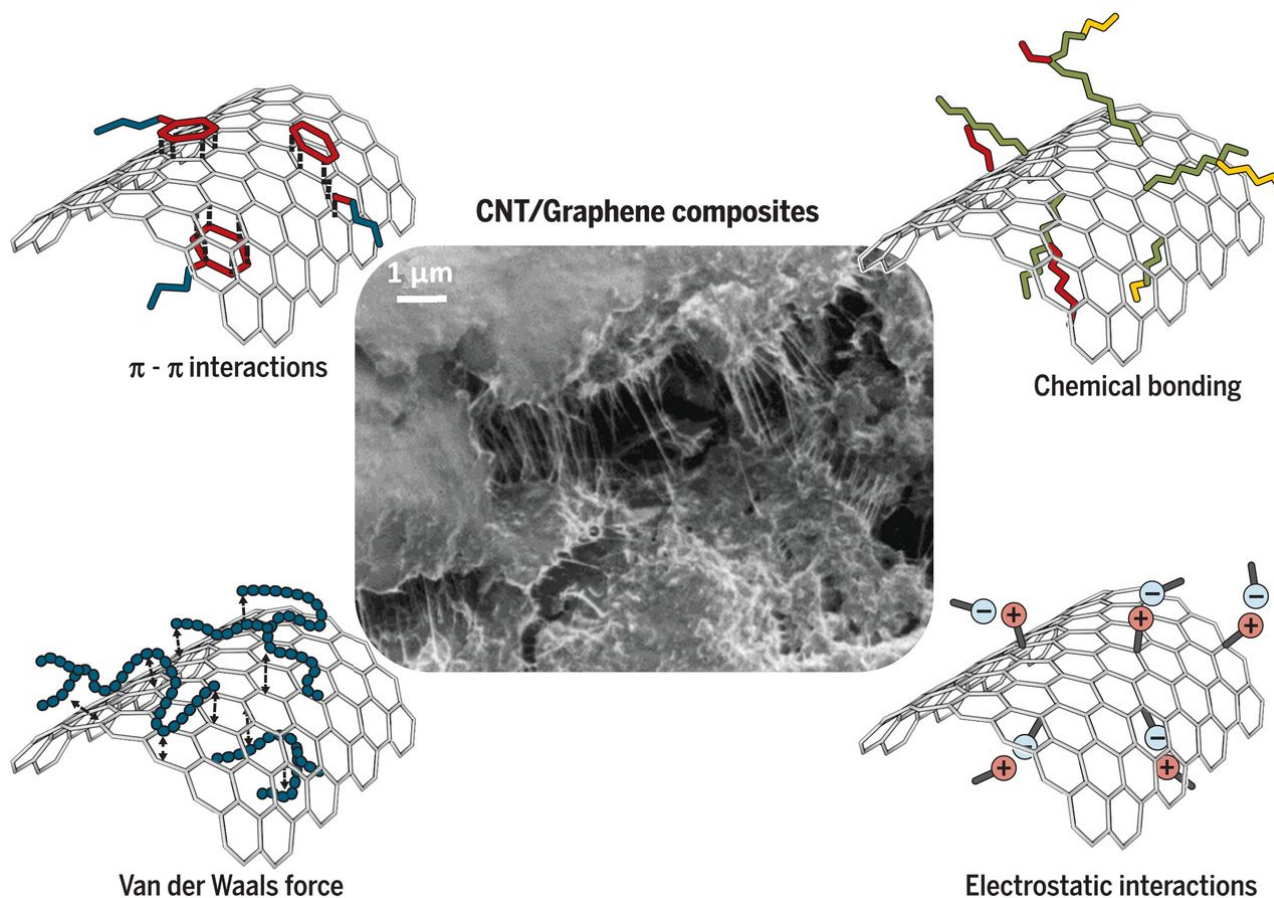


Figure 1: Schematic diagrams of four different chemical modification schemes of the interaction of CNTs or graphene with a polymer matrix [47]

optimizing the preparation process, Kuo-Hsiung Tseng *et al.* prepared the graphene with good dispersion by controlling the parameter of ESDM [34], further treatment is needed to play a better role in strengthening and toughening the ceramic substrate.

In previous research, Ian A. Kinloch *et al.* summarised four dispersion methods based on the combination mode between CNT/graphene and functional groups: π - π interactions, chemical bonding, as van der Waals forces and electrostatic interactions (as shown in Figure 1) [47]. This article proposes another classification method from a different view: covalent functionalisation and non-covalent functionalisation. Covalent functionalisation establishes covalent bonding between the nanocarbon and functional groups, which is more stable than the result of non-covalent functionalisation, and, according to Sagar Roy's research, covalent functionalisation can improve the mechanical properties of carbon nanotubes [35]. However, covalent functionalisation may destroy the structure of nanocarbon, because this method establishes covalent bonding by chemical reactions, such as acid corrosion

functionalisation and other methods, and decreases the effect of nanocarbon-reinforced ceramics [36–38]. Non-covalent functionalisation allows functional groups to be absorbed onto the surface of the nanocarbon via van der Waals bonds, π - π interactions, electrostatic attractions, and other phenomena between the groups and nanocarbon to promote dispersion without forming a chemical bond. This method can take full advantage of the effect of nanocarbon and preserve its structure [39–41].

2.1 Covalent functionalisation

The surface functionalisation of nanocarbon changes its surface characteristics and removes part of the van der Waals forces. Markandan *et al.* highlighted that the dispersion behaviour of graphene is predicted by the Derjaguin–Landau–Verwey–Overbeek theory, whose essence is the balance between van der Waals forces and electrostatic repulsion forces. The addition of surfactants counteracts the van der Waals forces and promotes graphene disper-

sion because of the high surface potential and strong electrostatic repulsion [32]. Walker *et al.* disperse graphene platelets (GPL) using cetyltrimethylammonium bromide (CATB) as the dispersant, which charges the matrix particles and graphene sheets. Because of the electrostatic repulsion among the same particles and the electrostatic attraction among different particles, the GPL is uniformly dispersed [42]. In the CNT–ZrB₂ composite, Wu *et al.* generate negatively charged CNTs by an acid treatment and maintain the pH value below 4. Accordingly, the composites are formed through electrostatic attraction between positively charged ZrB₂ and negatively charged CNTs, and after mixing, the composites are settled to produce a clear supernatant. It should be noted that there are no free multi-walled carbon nanotubes (MWCNT) in the supernatant to ensure that the CNTs do not aggregate during the mixture drying process [43]. In Al₂O₃ matrix composites, carboxyl (COOH[−]) adheres onto the surface of the CNT through CVD, and at the same time, Al(NO₃)₃·9H₂O electrolysis in (CH₃)₂NC(O)H can produce Al³⁺. Because of the combination of COOH[−] and Al³⁺, the CNT is dispersed uniformly [44].

After some existing experimental verification, the pH value, reaction time, and surfactant are three important factors that affect the dispersion of CNTs. If CNTs are dispersed by electrostatic repulsion, their surface charge density can be changed by controlling the pH value. When the pH value is over 3.7, the surface negative charge density increases with the pH value [26]. The longer the reaction time, the better is the dispersion effect of the CNTs. Considering that CNTs belong to the nanocarbon category, it is reasonable to believe that they provide a reference for carbon nanoparticles. Ahmad *et al.* emphasise that CNTs can thoroughly absorb a surfactant by prolonging the reaction time, and consequently, aggregation is resisted, which proves that the reaction time and surfactant are two factors that affect CNT dispersion [45]. Prolonging the reaction time can stimulate the dispersion of carbon nanoparticles and improve the properties of the materials; however, it may also diminish the strengthening effect of CNTs. Kasperski *et al.* find that covalent functionalisation may diminish the strengthening effect of MWCNT by destroying the structure of the MWCNT and thereby preventing them from producing crack bridging and other strengthening and toughening mechanisms [46]. Surfactants can influence the dispersion by changing the zeta potential on the surface of the CNT, for example, polyethylene amine provides the CNT with a positive surface charge, whereas sodium dodecyl sulfate provides it with a negative surface charge [46]. A. Kinloch *et al.* believed that chemical modification can facilitate the uniform dispersion of carbon

nanomaterials, prevent their aggregation, and improve the interfacial strength between carbon nanoparticles and ceramic matrix particles [47].

2.2 Non-covalent functionalisation

The most traditional non-covalent functionalisation is mechanical dispersion, such as ultrasonic treatment. Ultrasound can produce a strong shear force to disperse carbon nanoparticles in a liquid medium; however, this method can also damage the structure and reduce the aspect ratio of carbon nanotubes [23, 38, 48]. Therefore, the current research focuses on promoting nanocarbon dispersion by electrostatic interaction [42], hybrid particles [49] and designing the microstructures of ceramic matrix composites [50].

Concerning electrostatic interactions, CATB solution can disperse SWCNT because the hydrophobic SWCNT attracts the hydrophobic part of the surfactant, and then SWCNT is covered with positively charged surfactant molecules [42]. Sodium dodecyl sulfate (SDS) is also a good surfactant to disperse CNTs. The hydrophobic part of the SDS has strong adsorption onto the surface of the CNT. The charged head of the SDS molecule provides electrostatic repulsion to hinder CNT aggregation [51]. Sun *et al.* conclude that it is necessary for carbon nanotubes to be hydrophilic to disperse well in aqueous solutions [52].

Han *et al.* report that they use macroscopic CNT materials to promote dispersion [53]. Vertical, horizontal, and porous CNT materials have been used to prepare nanocomposites by direct infiltration, which can hinder the aggregation of CNT. Polyborosilazane penetration can invade the pores of CNT, and this can hinder CNT aggregation and fix the CNT in the original position so that the nanocomposites remain well-aligned even at high concentrations. Satam *et al.* found that when a MWCNT is embedded in an Al₂O₃ grain, a good dispersion effect is observed, as shown in Figure 2. Compared with the MWCNT at the grain boundary, the mechanical properties of MWCNT-embedded ceramic matrix composites exhibit excellent improvement [39].

Typically, in hybrid nanocarbon composites, there are two types of dispersion-promoting mechanisms. (I) One particle attaches to another particle, and these two particles hinder each other's aggregation [54]. (II) When two particles exist in a certain proportion, strong interaction will occur to form an interconnected network and hinder aggregation [51]. According to Tapasztó *et al.*, when preparing a GNP–Si₃N₄ composite, melamine could be easily embedded into graphene and produce a two-dimensional net-

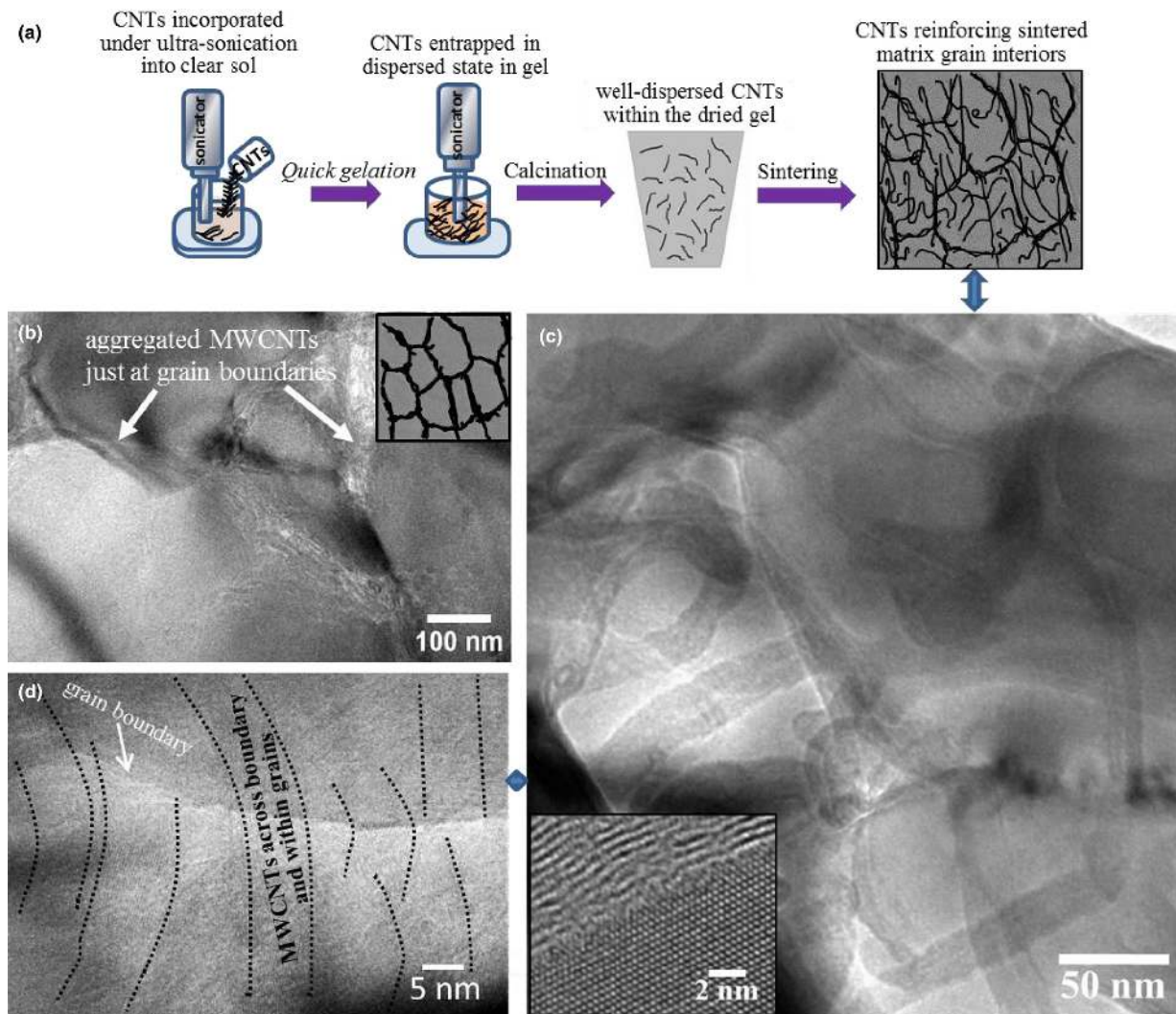


Figure 2: (a) The schematic diagram of the processing route and the ideal microstructural type with intergranular and intraparticle MWCNT; (b) the representative TEM images of "ball milling" and (c, d) "sol gel" Al_2O_3 -5vol%MWCNT. In c and d, we can see that the matrix particles exist in the MWCNT. (c) High-resolution images at the interface between MWCNT and Al_2O_3 particles in the matrix [39]

work among the graphene layers. As a result, the van der Waals forces among the layers are counteracted, so that the few graphene layers disperse uniformly. In the process, melamine will neither cause trauma nor form chemical bonds with the graphene scaffolds. Additionally, the surfaces of the materials form continuous GNP lubrication films and improve its frictional properties [49]. Akin *et al.* proved that the GNP microstructures that surround matrix particles can promote their dispersion and improve the relative density and mechanical properties of composites [55]. Yuan Gao *et al.* mentioned that GO can promote more stable dispersion of MWCNT due to their interactions, and they investigated the optimal ultrasonic dispersion parameters of GO/MWCNT in the dispersed cementing material [56].

2.3 Covalent and non-covalent functionalization combination

Covalent and non-covalent functionalisation each have their own advantages and disadvantages. Covalent functionalisation is extremely effective in adjusting the surface physical and chemical properties of nanocarbon. However, the experimental steps are considerably complicated and easily damage the nanocarbon structure. Non-covalent functionalisation is cost-effective and easy to operate; however, non-covalent bonding is relatively weak. To combine the advantages of both techniques, a new method that combines covalent and non-covalent functionalisation has been developed [57].

Ghobadi *et al.* dispersed CNTs uniformly by adding boehmite [41]. The boehmite formula is $\gamma\text{-AlOOH}$, which

is the precursor of $\gamma\text{-Al}_2\text{O}_3$. This formula has been widely used in composites, ceramic materials, protective coatings, and semiconductors [58–62]. The SDS charges the CNT surface negatively, and the stable sol of boehmite is a positively charged nanoparticle. When the two are mixed, boehmite adsorbs onto the surface of the CNT, resulting in four advantages to improve ceramic matrix composites [41]. (I) The density difference between the CNT and alumina particles will be reduced because the density of boehmite is higher than that of CNT. (II) Because CNT is trapped by matrix particles, its mobility decreases, which hinders aggregation. (III) The interface formed by the boehmite that adsorbs onto the CNT surface replaces the CNT–CNT and CNT–matrix interfaces, and the properties of the composites can be enhanced because the CNT–CNT interface is extremely weak. (IV) The boehmite on the CNT surface hinders the aggregation of CNT [63]. Chen *et al.* created a mixture of polyethyleneimine (PEI), tannic acid (TA), and MWCNT in aqueous solution at room temperature to produce TA–PEI–MWCNT [57]. It is found that the phenolic group of TA reacts with the amino group of PEI to form a cross-linked network, which is adsorbed onto the surface of the MWCNT. In the subsequent curing reaction, the PEI groups on the MWCNT surface react with the epoxy groups of epoxy resins to form covalent bonds. In this process, the advantages of covalent and non-covalent functionalisation are fully combined. First, the TA–PEI on the surface of the MWCNT can prevent MWCNT aggregation and minimise the damage caused to the MWCNT by the epoxy resins. Second, the reaction between the TA–PEI and epoxy resins enhances the MWCNT–epoxy resin interaction. Ma *et al.* produced a reaction between vinylcarbazole–glycidyl methacrylate and GNS [64]. The vinylcarbazole in VCz–glycidylmethacrylate absorbs onto the graphene surface by π – π interactions to promote the dispersion of the GNS. When epoxide reacts with the GNS, the interaction between the GNS and the epoxy matrix is enhanced. Through the combined covalent and non-covalent functionalisation mechanism, the GNS is dispersed uniformly.

3 Interface mechanism of nanocarbon reinforced ceramic matrix composites

The interface is the complex transition zone between the reinforcing phase and the matrix. Proper interface strength is the basis of strengthening and toughening

mechanisms, such as stripping, pull-out, and crack bridging. These mechanisms dissipate energy during the loading process [65–68]. It's worth noting that the best interface strength is not the strongest but the most appropriate. Some weak and strong interfaces are unable to reinforce ceramics [33, 69, 70].

3.1 Non-chemical combination

To obtain a certain interface strength, three key points are considered when designing the structure of nanocarbon: the surface roughness, the contact area, and the interaction between the nanocarbon and the matrix interface. Controlling these three factors means that the friction force or energy dissipation between the nanocarbon and the matrix can be controlled. How to control these factors remains an open question. Some specific methods of controlling these factors will be introduced in the next step.

- (I) The application of folds. In rGO– B_4C composites, Liu *et al.* find that the reinforcement effect of rGO with folds is extremely good. First, the graphene interfaces lids more easily than does the matrix causing weak graphene–ceramic interface bonding. Second, graphene with a high specific area can resist stress when it is interwoven to form a lubricant network, which performs an important function in enhancing the toughness of ceramic materials. Third, graphene sheets with folds can wrap the matrix particles more tightly, improving the interface friction and bonding to influence the local stress. Fourth, the folded rGO enhances the stress transfer through mechanical interlocking. Because of the above factors, the pulled-out graphene consumes more energy than do ordinary fillers and enhances the crack elongation resistance [29, 71]. In GNS– Al_2O_3 composites, the matrix contains folded and interconnected GNS. Under an applied load, the folded GNS plane slides along the base plane without any dislocation movement. Therefore, it is easy for cracks to propagate if the GNS is distributed along the grain boundaries, and as a result, an intergranular fracture is produced [72]. Folds can be formed by graphene lattice deformation, which is caused by attached functional groups (OH) or as a result of GNS stacking, accumulation during matrix grain growth, and reaction at the interface [73]. An ideal MWCNT that has a smooth surface is considerably easy to slide among the walls, preventing toughening behaviour. An imperfect MWCNT can provide effective

load transfer and improve the material strength and toughness [74]. Yamamoto *et al.* find that the surface morphology of MWCNT can be altered by acid treatment [75]. A certain degree of acid treatment will not destroy the MWCNT structure; however, it produces nano-pits in the local area. These pits are filled with matrix particles, which can fix MWCNT, forming mechanical interlocking, providing effective loading transfer and increasing the sliding resistance of MWCNT on the substrate [43]. Estili *et al.* report that the loading transfer at the interface between the MWCNT and the matrix is controlled by the interfacial shear mechanism, and the higher the interfacial shear resistance, the greater is the loading transfer [67], which originates from the structural unevenness between the MWCNT and the matrix, the mechanical interlocking, and the formation of chemical bonds at the interface.

- (II) The interaction between matrix grains and nanocarbon. Recent studies show that nanocarbon embedded into matrix particles, rather than at the interface, may also yield a better reinforcing effect [76]. Ahmad *et al.* show that if the matrix cracks, the CNT located at the grain boundary and closely connected to the matrix will undergo elastic deformation, which enhances the energy dissipation [68]. Liu *et al.* find that when graphene is anchored at the grain boundaries of matrix particles, these particles (adjacent to graphene) exert stress on the graphene, causing it to bend and embed among the particles. Then, the bond between the matrix particles and graphene becomes closer, increasing the contact area and enhancing the friction [65]. Wu *et al.* prepare a multi-layered structure with a micron-sized length at the grain boundary of ZrB_2 called a grapheme nanoribbon (GNR). The GNR may be formed by the chain-breaking and collapse of MWCNT under the influence of residual stress or during the grain growth, and it deflects cracks into a tortuous path, which extends the crack length and reduces the stress concentration to consume the fracture energy [43, 77]. Graphene has self-lubricating properties. The circular grains appearing in the composites will promote deformation or sliding among the grains because circular grains are easier to slide than are faceted grains [72]. In addition, the MWCNT can provide three-dimensional channels to promote the grain boundary pinning effect, delay grain growth, induce densification and release residual stress [43]. Ahmad *et al.* prepare CNT- Al_2O_3 composites and find that the CNTs are not only at the

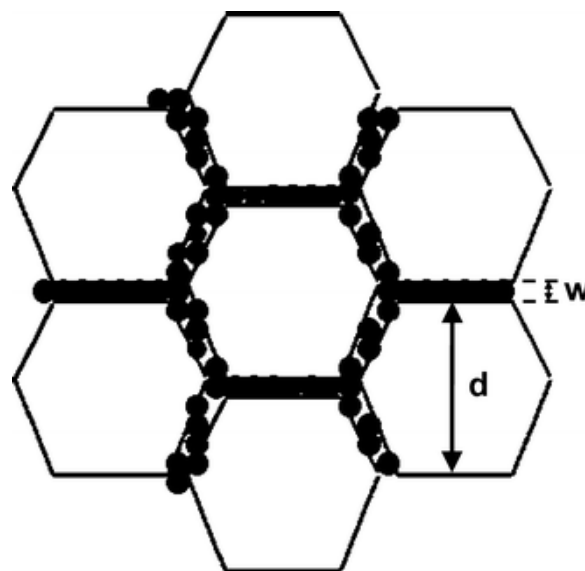


Figure 3: 2D model of SWCNT and Al_2O_3 particles [80]

grain boundaries but are also within the grains [78]. After CNTs are embedded into alumina particles, they are compressed radially and tensile stressed circumferentially during sintering and cooling because their thermal expansion coefficients differ from that of the matrix. Therefore, the cracks caused by processing are attracted to CNT through circumferential tension, which reinforces the composites. However, if the CNT is only embedded in grains with short lengths, it will not produce a strengthening effect [4]. In addition to the above common mechanisms, in the study of HaibaoLu *et al.*, the crack propagation inside the multi-layer nanocomposites is observed and the composites of multi-layers of the nanopaper and SMP (shape memory polymer) matrix have four interfaces enhancing the interface bonding. This seems to be another idea to improve interface [79].

- (III) The contact area between the nanocarbon and matrix. Zapata-Solvas *et al.* study the distribution of SWCNTs along the grain boundary of Al_2O_3 and establish a model with which to express the contact ratio between SWCNT and Al_2O_3 particles, as shown in Figure 3 [80].

Assuming that the SWCNT is uniform, the average grain size of hexagonal grains is denoted as 'd', the height is 'L', the average diameter of the SWCNTs is 'w', and the number of SWCNTs in each hexagon is 'n'. The volume fraction of SWCNTs can be expressed as follows.

$$f = \frac{n\pi w^2}{n\pi w^2 + \frac{\sqrt{3}}{2} d^2} \quad (1)$$

The surface fraction of Al_2O_3 grains that come into contact with the SWCNT is calculated by the following.

$$A = \frac{n\pi w}{2d\sqrt{3}} \quad (2)$$

The interfacial strength of composites should not be extremely high. Shirasu *et al.* mention that a high-interfacial strength matrix will fracture MWCNTs because the load on the MWCNTs exceeds the limit, and the energy consumption during pull-out will be reduced [33]. Appropriate interfacial strength reduction can ensure that the MWCNTs are pulled-out before the fracture to achieve the reinforcement of composite materials [33]. Bocanegra-Bernal *et al.* also explained that extremely strong interface bonding will yield brittle ceramics [23]. Sometimes, choosing carbon nanoparticles differing from the matrix in terms of thermal expansion coefficients will cause interface mismatching, reducing the interface strength during sintering [25]. The interfacial strength of composites can be approximately calculated based on the protruding a nanocarbon length. Shirasu *et al.* studied the relationship between the protrusion length and the interface strength [33]. According to the assumption of Kelly–Tyson, the relationship can be expressed by the following equation:

$$\tau_i = \frac{r\sigma_{CNT}}{L_C} = \frac{r\sigma_{CNT}}{4L_f} \quad (3)$$

In this formula, r is the MWCNT radius, σ_{CNT} is the MWCNT tensile strength, L_C is the critical maximum MWCNT length, and L_f is the prominent length.

Finally, the effect of defects on the interfaces of composites should be noted. Voids should be taken seriously in graphene-toughened composite investigations. The voids will promote the initiation of cracks under lower loads and reduce the strength [81]; however, Michálek *et al.* noted that the effect of 0–2% porosity on the mechanical properties of MWCNT– Al_2O_3 – ZrO_2 composites can be neglected [1]. The effect of introducing a point defect on τ_b is reported as follows:

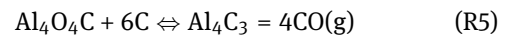
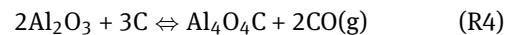
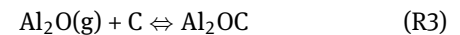
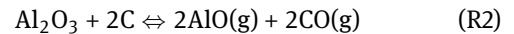
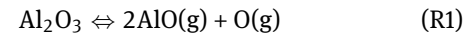
$$\tau_b = \frac{F_{\max}}{2\pi r l_{emb}} \quad (4)$$

Where F_{\max} is the maximum measuring force applied to the CNT and l_{emb} is the length of the CNT embedded in the matrix. This formula can provide an effective strategy for improving nanocarbon-reinforced ceramic matrix composites [82]. But in boron nitride sheet, it will result in a sharp decrease in mechanical performance when defect percentage is greater than 1% [83]. Xia *et al.* explained that the elastic modulus of composites will decrease because of the low elastic modulus of rGO and the presence of voids [71]. When reinforcement phases (such as GPL or

CNT) do not tightly bond with the matrix, voids may form at the interface [65]. Because of differences in thermal expansion coefficients and shrinkage ratios of the interface between the reinforced phase and ceramic matrix during the cooling process, the contact area between the reinforcement phase and matrix will be reduced, cracks will initiate easily, and the strength of the composites will be reduced. It has been found that there more holes are formed at the interface between thick GPL and a ceramic matrix because the toughness of thick GPL is lower than that of thin GPL. However, some studies show that a certain number of voids in rGO is beneficial to enhancing the interface bonding. Because rGO has more wrinkles and defects than do graphene sheets, its defects can enhance the chemical interaction with B_4C grains [29]. More attention should also be focused on the change in the shape of graphene particles.

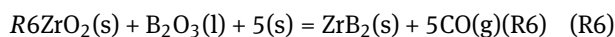
3.2 Reaction bonding

Reaction bonding is a method of enhancing the interface by chemical reactions. Normally, there are two methods: one is removing the included oxide through chemical reaction, and the other is establishing covalent connections between the nanocarbon and matrix. Generally, inclusions at the interface will affect the interfacial strength of composites. These inclusions can be removed by chemical reaction with nanocarbon, improving the interfacial bonding degree [84]. GPL can use its self-lubrication characteristics to stimulate the rearrangement of B_3C particles, and it can remove oxide inclusions through interfacial reactions. The two characteristics can tightly bond the interface of GPL and matrix to strengthen and toughen composite materials [85]. Ahmad *et al.* found the following reactions at the CNT– Al_2O_3 interface [68].



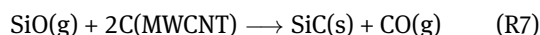
It is difficult for materials to diffuse and form a meso-phase if they are rapidly sintered through a high-frequency induction heating sintering (HFIHS) process; hence, the above

reaction will not occur [72]. In addition, Ahmad *et al.* explained that Al_2O_3 has high chemical compatibility with the CNT and matrix and can transfer loads well, and accordingly, the high elasticity of CNT is used fully [45]. Asl *et al.* reported that in composites, oxides not only reduce the density of ceramics but also stimulate grain growth. Graphene can eliminate oxidised impurities through interfacial reactions. Chemical reactions exist in SiC-ZrB_2 composites to eliminate impurities produced by oxidising [86].

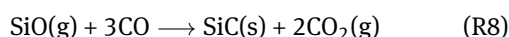


In some situation, chemical reactions may be adverse. The reaction between GPL and preheated ceramic during high-temperature pyrolysis will reduce the interface strength because the pre-ceramic with remarkable viscosity and fluidity can reduce the resistance of the impregnation process, promoting dispersion [87]. A macroporous graphene network solves this problem by reducing the tolerance of the impregnation process. Additionally, a ceramic slurry can hinder the reaction [87].

In addition, chemical bonds can be formed by the reaction between carbon nanoparticles and the matrix to enhance interfacial bonding. The functional groups on the initial GO surface can promote better interface bonding between the outer layer of rGO laminates and ceramic surfaces [66]. Zeng *et al.* found that the Zr-O-C chemical bond is formed at the interface of GO-ZrO_2 composites [88]. This is attributed to the formation of large oxygen vacancies at the bottom of ZrO_2 upon sintering doping with rare earth (yttrium oxide) under a high-vacuum and anoxic atmosphere. Then, the unstable oxygen vacancies disappear after being filled with oxygen because they break the C-O-H hydrogen bond. The chemical bond will lead to more energy consumption during crack propagation and improve the fracture toughness of composites. When Morisada *et al.* prepare MWCNT-SiC composites, the adhesion between the MWCNT and matrix is improved by coating the MWCNT with SiC [89]. First, the surface of the MWCNT transforms into SiC, and thereafter, nano-sized SiC is deposited in a thin SiC layer. A thicker SiC layer can be obtained through the following reaction.



The original surface of the MWCNT is extremely smooth, but several SiC particles can form on the MWCNT surface by the following reaction.



Through this reaction, the MWCNT surface becomes rough, and the mechanical properties of the composites are en-

hanced. Jung-Hoo *et al.* find that in $\text{SWCNT-Al}_2\text{O}_3$ composites, forming a C-O-Al (or COOAl) bond without any interfacial phase promotes tight bonding between SWCNT and Al_2O_3 grains [90]. Wozniak *et al.* prepare surface-modified $\text{rGO-Al}_2\text{O}_3$ composites. It is found that the mechanical properties of the composites exhibit better results than do $\text{GO-Al}_2\text{O}_3$ composites without surface modification [91]. The interfacial adhesion of modified composites is good, which effectively prevents the formation of voids at the interface and improves the mechanical properties of composites. However, in GO without modification, the interface bonding strength is further reduced because of the pores caused by differences in thermal expansion coefficients.

3.3 Interfacial microstructure and formation principle

The unique structure formed by carbon nanoparticles in composite materials has a good effect on strengthening the interfacial bonding of composite materials. Huang *et al.* mention that laminated composite materials can improve mechanical properties [92]. In their experiments, the GO layers are distorted and deflected between the SiC grains during hot pressing without being destroyed. The rGO layers deform because the extrusion during the sintering process dissipates the fracture energy by prolonging the propagation path of the fracture, which improves the flexural strength and toughness. However, other studies show that layered structures may reduce the mechanical properties of composites. Zhao *et al.* report that the laminar structure in GNP-BCP composites reduces the mechanical properties [93]. Because of the external pressure and powder flow during the HP, the GNP is distributed along the direction perpendicular to the HP. When a crack encounters the GNP, it may propagate along the interfaces among the GNP layers or between the GNP and BCP matrices; however, the GNP will not be pulled out, which can limit its toughening effect. Zeng *et al.* mention that when graphene aggregates into several layers, cracks will penetrate it to reduce the energy consumption so that the pulling-out effect of graphene is reduced. Although more layers can reduce the defect concentration, the more layers of graphene that aggregate, the less energy is consumed [88]. Micháľková *et al.* explain that the Young's modulus of graphene containing several layers is considerably lower than that of single-layer graphene, and the Young's modulus significantly influences the fracture toughness of composites [94]. Generally, the modulus of CNTs are scaled according to their length, so scholars have stretched pre-CNT to enhance its strength [95, 96]. Han *et al.* report that 3D CNT scaffold re-

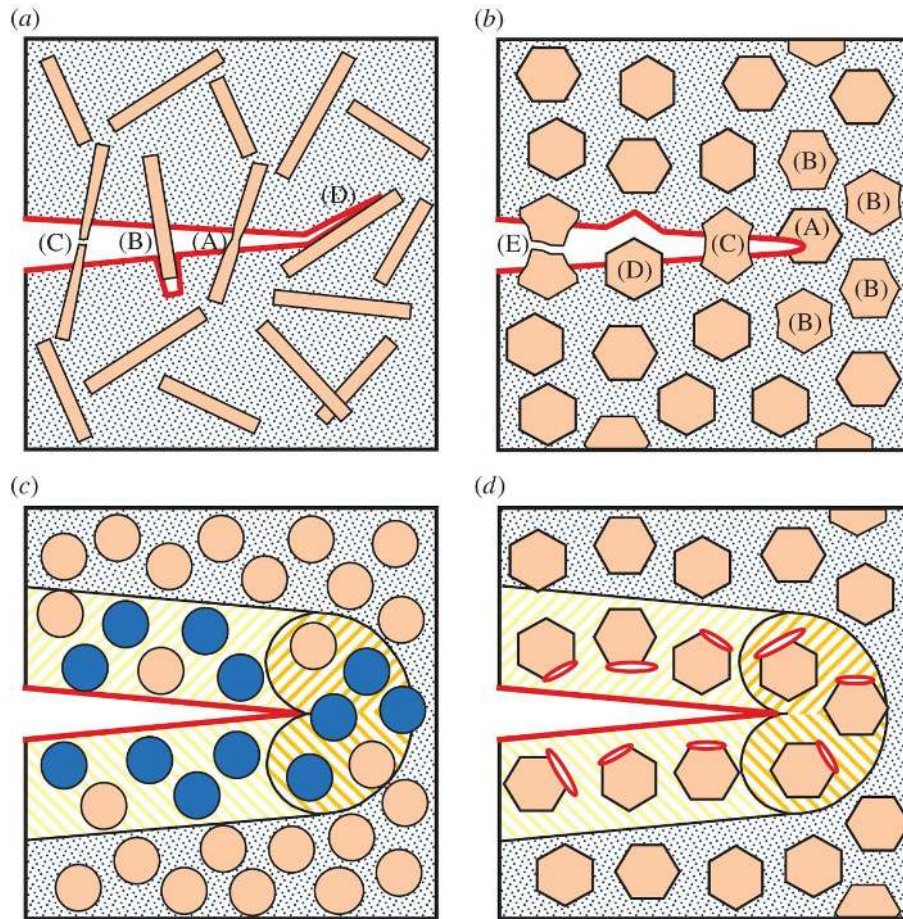


Figure 4: (a) The transformation of the tetragonal phase into the monoclinic phase; (b) Microcrack toughening [99]

inforce SiC–BCN composites [53]. Numerous CNT bundles are observed, and certain parallel CNT bundles are at the root of the vertical bundle. These single CNT bundles exhibit a 3D structure. There are three steps in the fracture process: (I) crack initiation and bridging; (II) pulling out of the CNT bunches; and (III) crack propagation and CNT bunch fracturing. In step (I), the cracks propagate along the interface between the parallel bunches and the matrix. In step (II), in order to bear the maximum loading and pull out from the matrix, the parallel CNT bunches begin to align along the stress direction, and fractures rarely occur during this process. Only when the stress exceeds the strength of the CNT do the CNT bunches fail because of the strong bond between the CNT and ceramics. The 3D structure makes full use of the strength and toughness of the CNT, increases the interfacial shear force, improves the stress transfer and realises stress distribution on a single CNT [53]. However, if the graphene filler exceeds the permeability limit, then it will form a three-dimensional network that will cause failure of the bridging mechanism and reduce the properties of the composite material [97].

Ramirez *et al.* find that when cracks are bridged, smaller rGO layers are pulled out and larger rGO layers strongly bond with the matrix because of its ripples and extremely high aspect ratio, which can provide highly effective crack wake bridging and extraordinary rGO nanocomposite toughness [66]. For the aspect of bridging, the rGO should be as small and thin as possible to improve the fracture toughness because the smaller the GO is, the more graphene materials are used to bridge cracks in the same volume fraction [98]. However, Ovid'ko *et al.* explained that graphene with a wide width, extensive length, and high strength effectively improves the energy dissipation associated with plastic deformation during the pull-out process, because cracks cannot penetrate graphene, and the geometrical shapes of graphene indicate that they are difficult to pull out; therefore, the effective energy dissipation associated with plastic deformation during the pull-out process aids in improving the toughness (Figure 4) [99].

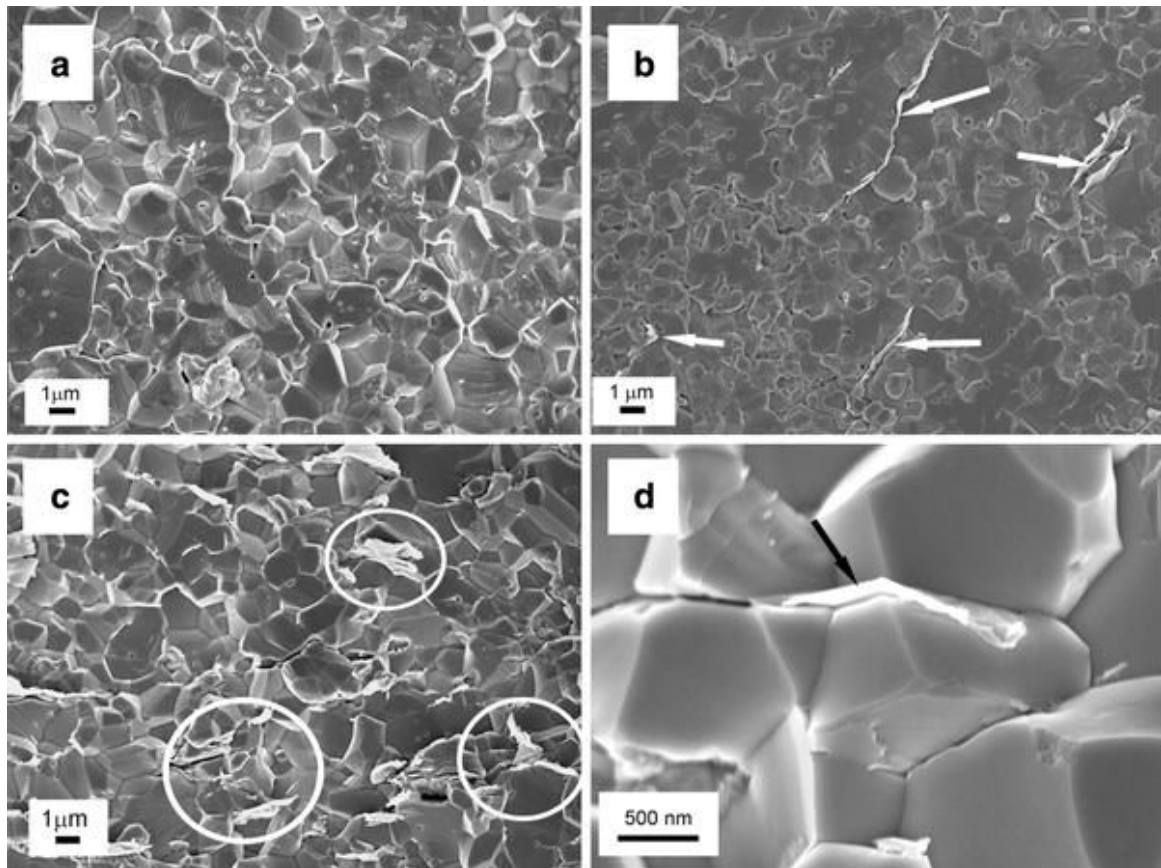


Figure 5: (a) Al_2O_3 ; (b) Al_2O_3 -0.75 wt% GNP; (c) GNP winding around Al_2O_3 grains [2]

4 Toughening mechanisms of nanocarbon toughened ceramic matrix composites

4.1 Fine-grained strengthening

Fine-grained strengthening is a method commonly used for nanocarbon to strengthen and toughen composites [2, 100–103]. Nanocarbon is usually located at the grain boundary, allowing it to provide a pinning effect, which can not only promote nanocarbon dispersion but also inhibit grain growth. According to the Hall–Petch formula, the strengthening effect of grain refinement is extremely evident. There are three important factors that influence the effect of fine-grained strengthening: the geometric shape, the content of nanocarbon, and the temperature and oxide impurities.

$$\sigma_s = \sigma_i + kd^{-\frac{1}{2}} \quad (5)$$

The first influencing factor is the nanocarbon content. Ahmad *et al.* mention that the grain size of Al_2O_3 will sud-

denly decrease with the addition of a low amount of CNT. The decrease is mainly caused by the grain boundary pinning effect. However, the grain size won't decrease unceasingly as the content of CNT increases because the CNT concentration only increases at the grain boundary; however, this does not increase the number of pinned boundaries [45]. Shin *et al.* found that the grain size of Al_2O_3 decreases with the increase of the rGO amount, as long as they are uniformly dispersed in SWCNT-rGO- Al_2O_3 composites [90]. Therefore, the number of pinned boundaries can be increased by promoting nanocarbon dispersion.

The second influencing factor is the geometric shape. rGO refines Al_2O_3 grains better than does SWCNT because its geometric shape is more favourable for the grain boundary pinning effect [90]. Apart from the pinning effect, nanocarbon (graphene, GO, rGO) winding at grain boundaries can effectively inhibit grain growth and promote dispersion [2, 104]. The winding mechanism is attributed to the large specific surface area of nanocarbon. In addition, as presented in Figure 5, this mechanism not only refines grains but also increases the energy consumption during pulling out. Furthermore, it increases the contact area between the GNP and matrix particles [2]. Inam *et al.* report

that CNTs form a strong entanglement network in CNT– Al_2O_3 composites to hinder the grain growth, such that the grain size of Al_2O_3 is reduced by approximately 10 times, and the properties of the composites can be improved [105]. Yamamoto *et al.* compared MWCNT– Al_2O_3 composites before and after acid treatment. They find that acid treatment does not change the grain refinement of MWCNT in Al_2O_3 particles [75]. Liu *et al.* reported that GNS with a large specific surface area can effectively inhibit grain growth. It is found that TiC particles practically stop growing in the presence of thin GNS [106]. The ratio of the GNS size is the most important factor hindering the grain growth. If the ratio is extremely small, grain boundary migration will not occur, and grain growth will be prevented. Therefore, a thin-layer structure is more effective in inhibiting grain boundary migration than is a cubic structure of the same volume. On this basis, the proportion required for completely preventing the grain growth is investigated.

$$\bar{D} = \frac{d}{V_d} \quad (6)$$

In the above equation, \bar{D} is the average grain size, and d and V_d are the second-phase particle size and volume content, respectively.

The third influencing factor is the temperature and oxide impurities. Sedlk *et al.* showed that high-temperature hot pressing usually results in grain coarsening [107]. Asl *et al.* mentioned that oxide impurities not only hinder densification but also promote grain growth [86]. However, these oxide impurities can be removed through interfacial reactions. Yavas *et al.* highlighted that the faster the heating rate, the smaller will be the grain size [108]. Cryogenic high-pressure preparations can inhibit grain growth [29].

4.2 Second-phase strengthening

In nanocarbon ceramic matrix composites, second-phase strengthening produces a great effect, and it mainly plays the role of crack deflection. Crack deflection or crack bifurcation may occur when a crack encounters nanocarbon. When the crack propagates in the matrix and encounters nanocarbon, the nanocarbon will usually deflect the crack at a certain angle. In this way, the crack-propagating fracture energy is consumed, the crack-propagating rate is reduced, and the toughness of the composite is enhanced [100]. Ming Lei *et al.* studied the obstacles of fillers on the crack propagation in detail [109]. Another common mechanism is crack bifurcation, which occurs at the graphene–ceramic interface when crack propagation encounters graphene sheets [87, 110]. The main crack

extends along the vertical direction, and the bifurcation crack extends along the graphene–ceramic interface. The bifurcation crack is terminated when a micro-crack is formed at the end of the interface and can be deflected at 90° to extend to the ceramic matrix, which benefits the stress propagation at the corner. Afterward, the new crack propagates parallel to the main crack. When the graphene sheets are distributed horizontally, the new crack will deflect along the sheet and then converge with the main crack. If the new crack deflection encounters only one graphene sheet, a quadrilateral crack propagation path will appear. A polygon deflection path will appear when the crack encounters multiple layers of graphene. With continuous crack bifurcation, the crack propagation path considerably extends, consuming fracture energy and improving the toughness of the composite [87, 110]. In addition, when the second-phase particles wrap around the matrix particles, a continuous graphene wall will form along the grain boundary, and this can change the direction of the crack as it propagate from two-dimensional to three-dimensional space (Figure 6) [42]. If the second-phase particle size is extremely small, then crack deflection will not become the primary toughening mechanism [111].

In some situations, second-phase strengthening plays another role. When the uniformly dispersed second-phase particles are firmly bound to matrix particles, the stress can be transferred among the grains, and the failure mode can be changed to transgranular fracturing [72]. Nisar *et al.* reported that the addition of second-phase particles causes interfacial stress, enhances the integrity and toughness of the structure and reduces the tensile stress acting on the matrix, which improves the toughness [112]. Ramirez *et al.* revealed that under a strong confined shear field of the indenter, shear fracture may occur along the graphene– Si_3N_4 interface at the contact damage zone and prevent the formation of long cracks [70]. Ipek *et al.* investigated TiB_2 – SiC –GNP composites and find that the GNP effectively strengthen and toughen the composites when they surround matrix particles. In addition, strengthening and toughening mechanisms (such as crack deflection, branching, and SiC pull-out) are observed in the composites [55]. The matrix particles surrounded by graphene can connect the graphene to several matrix particles and form complex anchorage to provide higher interfacial resistance and increase the energy required for graphene pull-out [72]. The GPL is pulled out from the matrix not only by cracking but also when the graphene layers of GPL slide, decreasing the toughening effect [111]. Ming Lei *et al.* added MWCNTs/CNFs with skeletal structure to the polymer polystyrene and studied the micro-motion mech-

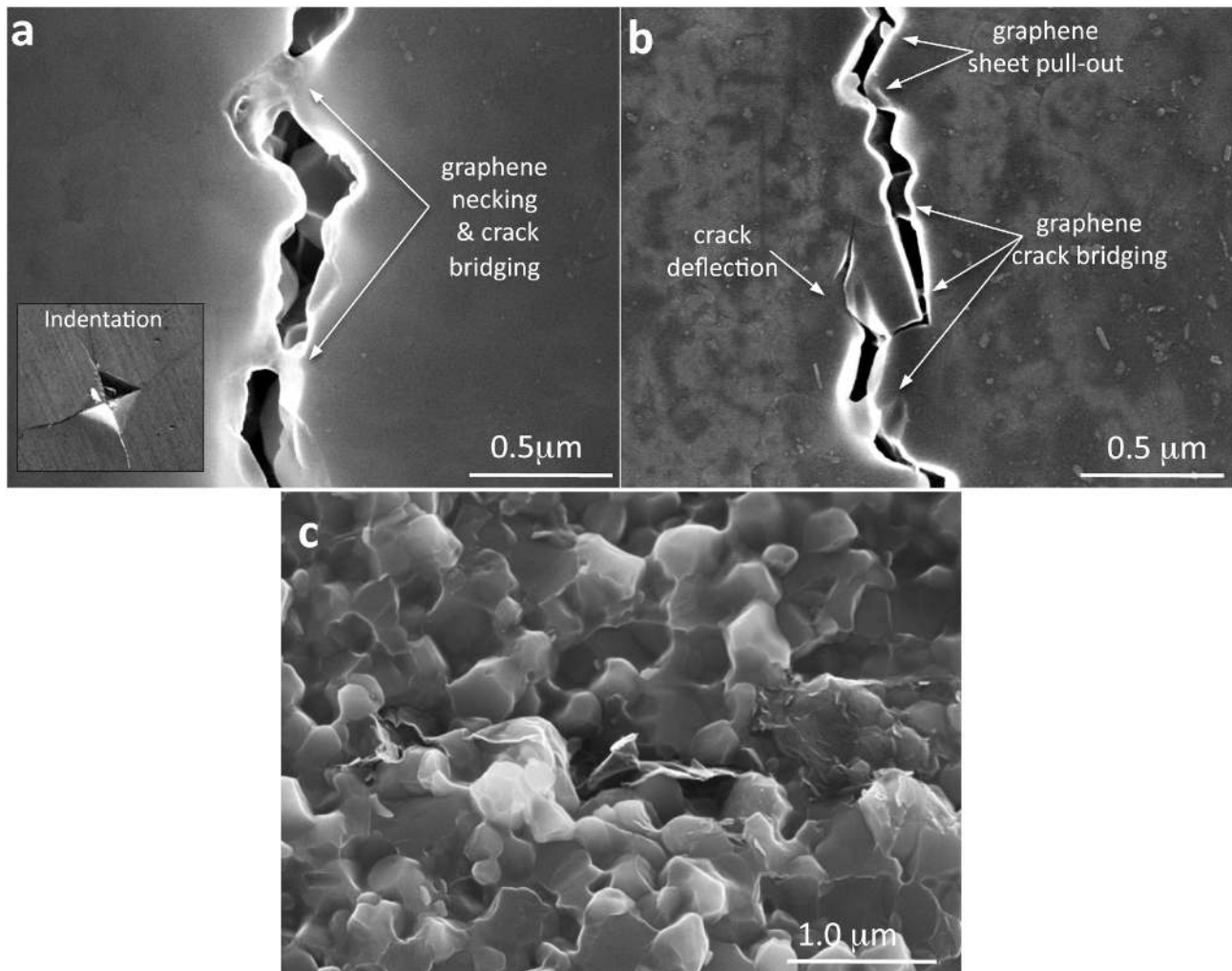


Figure 6: Toughening mechanisms in GPL-Si₃N₄ nanocomposites. (a) Micro-hardness testing resulting in a crack. (b) Crack following a tortuous crack propagation path. (c) 3D toughening mechanisms of the GPL-Si₃N₄ nanocomposite [42]

anism insides the CNT/CNF composite system to explain the reason of improvement of mechanical properties [113].

4.3 Pull-out and bridging mechanisms

Pull-out and bridging are common reinforcement mechanisms in nanocarbon-reinforced ceramic matrix composites [80, 97, 114–116]. Crack bridging occurs during matrix cracking. The crack surface is connected by the two ends of the nanocarbon. As the distance between the two walls of the crack increases, the nanocarbon begins to deform. During the whole process, the two segments of nanocarbon are closely attached to the matrix and consume the crack propagation energy. Before reaching the deformation limit of the nanocarbon, a pull-out may arise and consume the fracture energy, or nanocarbon debonding accompanied by crack bridging may occur. In this process, defects will

affect the movement of carbon nanotubes and further affect energy dissipation, Xiaotian Lin *et al.* studied this phenomenon [117]. Ramirez *et al.* investigated the condition of elastic mismatching and find that debonding occurs when the interface port area is less than 1/3 of the fracture energy of grapheme [97]. Mukhopadhyay *et al.* stated that ex-foliation occurs in the matrix, not at the MWCNT–matrix interface [115].

Ahmad *et al.* reported the energy absorption of CNTs during the pull-out process [45]. On the premise that the two ends of the CNT are firmly connected with the matrix particles, the CNT can bear 40% of the strain before fracturing when the material undergoes deformation. When the material deformation exceeds the maximum load that the CNT can bear, the CNT will collapse. In this process, the CNT absorbs a considerable amount of energy because of its high elasticity modulus and deformation ability, im-

proving the toughness of the composite. The key in this enhancement mechanism is the strong interface between the CNT and matrix. The pull-out toughening mechanism of the GNS is extremely complex and involves several processes. The outermost layer of the GNS tightly bonds with the matrix, and it consumes a significant amount of energy during crack propagation. After the matrix rupture, the load transfers to the inner part of the GNS. Because of particle entanglement, the inner GNS is fixed in the matrix. After deformation, it may disentangle from the matrix. Finally, the broken GNS layer can cause a stick–slip phenomenon of carbon atoms under the interlayer friction during movement [73]. Similarly, MWCNT has an analogous mechanism. Estili *et al.* discover the multi-wall failure mechanism of the MWCNT in MWCNT–Al₂O₃ composites during the crack-bridging process [118]. They report that when the crack passes through the MWCNT, the MWCNT can bridge the crack and deflect it around the radial interface of the MWCNT. Subsequently, the MWCNT bridges the crack and bears the applied load by means of strong interfacial shear resistance. This approach transfers the load not only to the outermost wall but also to the inner wall. Thus, it significantly improves the carrying capacity of the MWCNT. It should be noted that this high-energy dissipation multi-wall failure can only be achieved in the absence of holes and 3D structures. Recent studies report that ultralight nanoporous graphene with 3D structure has great potential for toughening ceramic-based materials because of its high strength and elastic modulus [119, 120]. In addition, Wu *et al.* explain that in composites, the thermal mismatch compressive stress caused by sintering results in the radial deformation of the MWCNT, causing the inner wall to bear the load and greatly improving the bearing capacity of the MWCNT [43].

4.4 The joint action of multiple mechanisms

When several mechanisms act collectively, the mechanical properties of composites can be greatly improved [93]. In GNP–BCP composites, crack deflection and branching or crossing of the GNP may occur when crack propagation encounters the GNP. After crossing the GNP, the interface along the crack propagation path will peel off. These effects can extremely prolong the crack propagation path and consume the energy of crack propagation. Finally, when the crack completely crosses the GNP, crack bridging will occur, and the energy of crack propagation will continue until the GNP breaks or is pulled out. When the driving force of crack propagation is insufficient, it will stop earlier.

However, when the GNP is not parallel to the stress direction for bridging, the GNP will bend at the crack point in the matrix, leading to premature failure of the crack surface and preventing the GNP from being pulled out. It should be noted that when the GNP is parallel to the direction of crack propagation, a series of strengthening mechanisms will not work [115]. Bahareh *et al.* reported the synergistic enhancement of CNTs and GNPs in GNT(GNP+CNT)–Al₂O₃ composites [121]. It is found that the CNT is embedded in the surface of the GNP sheets and exists around the grain boundary, which makes the CNT bind to the matrix interface closely, hinders grain growth, inhibits grain boundary movement and changes the fracture mode from intergranular to transgranular fracturing. The GNPs and CNTs produce the effects of grain refinement and interface strengthening, respectively. The GNP tightly bonds with the Al₂O₃ grains because of its flexibility and large interface area, increasing the interface friction between the GNP and matrix and promoting the consumption of energy required to pullout the GNP during the fracture process. Because of its high aspect ratio, the CNT stretches longer than does the GNP during the collapse; hence, it provides a contribution to bridging the matrix grains. Consequently, the two mechanisms work together to significantly improve the properties of composites.

5 Research prospects

Some progress in nanocarbon-reinforced ceramic matrix composites has been achieved so far; moreover, the potential of improving mechanical properties has also been presented. Currently, studies on nanocarbon-reinforced ceramic matrix composites focus on improving the fracture toughness of the composites by improving the preparation methods, interfacial bonding, and design of microstructures. However, the problems that involve the aggregation of carbon nanoparticles and weak interfacial bonding remain unsolved. In this paper, the research progress of nanocarbon-reinforced ceramic matrix composites is reviewed. The mechanisms of strengthening and toughening nanocarbon-reinforced ceramic matrix composites–nanocarbon dispersion, interface bonding and the micro-toughness mechanism of nanocarbon-reinforced ceramic matrix composites–are summarised.

(1) Carbon nanoparticle dispersion mechanism

Because of its high aspect ratio, surface energy and van der Waals forces, nanocarbon easily aggregates, which critically affects the mechanical properties of composites. At present, the surfaces of carbon nanoparticles can be charged by covalent functionalisation to hinder the aggregation caused by van der Waals forces, which makes the nanocarbon disperse better. For example, covalent functionalisation can be achieved by the preparation of hybrid carbon nanocomposites. It is expected that the combination of covalent and non-covalent functionalisation may be improved and become a better method in the future. Well-dispersed nanocarbon can allow the complete development of strengthening and toughening mechanisms, including fine grain strengthening, second-phase strengthening, pull-out, and bridging in the ceramic matrix. As a result, the properties of ceramic matrix composites can be significantly improved. However, when nanocarbon is aggregated or not uniformly dispersed, it not only fails to enhance the mechanisms but also produces defects in the composites, causing stress concentration or matrix splitting, which reduces the mechanical properties of composites. Therefore, the good dispersion of nanocarbon is the foundation of nanocarbon-reinforced and-toughened ceramic matrix composites.

(2) Interface mechanism design

In controlling the interface of ceramic matrix composites, attention should be focused on determining the proper interfacial strength. When the interfacial strength is extremely low, interfacial debonding can easily occur during the pull-out and bridging processes. Consequently, strengthening and toughening mechanisms will be unable to perform their supposed functions. If the interface is extremely strong and if a considerable difference between the elastic modulus values of the carbon nanoparticles and matrix exists, then cracks will form and propagate rapidly in the cross-section, thereby leading to brittle fracturing. In this situation, there will be no additional energy consumption, and the nanocarbon will not be able to perform its strengthening and toughening functions. To achieve a good interface bonding in ceramic matrix composites, it is imperative to control the contact area, surface roughness and interface bonding. In mechanical bonding, nanocarbon has a large specific surface area and extreme surface roughness, so it can promote interfacial bonding by embedding in the matrix grain and through the for-

mation of 3D scaffolds. In reaction bonding, it can also promote interfacial reactions to remove oxide inclusions upon increasing the heating temperature and prolonging the heating time, which can either further promote interfacial bonding or induce the formation of chemical bonds among the carbon nanoparticles (which react with the matrix).

(3) Strengthening and toughening mechanisms

Among nanocarbon-reinforced ceramic matrix composites, the common mechanisms are fine-grained strengthening, pull-out strengthening, bridging strengthening and second-phase strengthening, which are based on good nanocarbon dispersion. The above mentioned mechanisms substantially increase the energy dissipation during material fracture. For pull-out strengthening and bridging strengthening, better interface bonding is necessary. If the interface bonding is extremely weak, then debonding will occur. The combination of various mechanisms produces excellent strengthening effects, which require good carbon nanoparticle dispersion and strong interfacial bonding in composites. Graphene and CNTs have distinct differences in terms of strengthening and toughening ceramic matrices. Although both can perform well in grain refinement, CNTs can only hinder grain growth, whereas graphene can hinder grain growth and wraparound the grains, which indicates that graphene can refine grains better than can CNTs. In addition, the CNTs tend to produce pull-out and bridging effects that are stronger than those of graphene. From another aspect, graphene is more effective in promoting crack deflection because of its large specific surface area. When both of these materials work together, the optimal strengthening and toughening effect can be achieved in all stages. In the process, graphene performs a major function in grain refinement and crack deflection, and the CNTs perform better in bridging and pull-out. Accordingly, the ideal strengthening and toughening effects can be achieved.

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