Review

Recent Developments in Carbon Nanotubes-Reinforced Ceramic Matrix Composites: A Review on Dispersion and Densification Techniques

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Abstract: Ceramic matrix composites (CMCs) are well-established composites applied on commercial, laboratory, and even industrial scales, including pottery for decoration, glass–ceramics-based light-emitting diodes (LEDs), commercial cooking utensils, high-temperature laboratory instruments, industrial catalytic reactors, and engine turbine blades. Despite the extensive applications of CMCs, researchers had to deal with their brittleness, low electrical conductivity, and low thermal properties. The use of carbon nanotubes (CNTs) as reinforcement is an effective and efficient method to tailor the ceramic structure at the nanoscale, which provides considerable practicability in the fabrication of highly functional CMC materials. This article provides a comprehensive review of CNTs-reinforced CMC materials (CNTs-CMCs). We critically examined the notable challenges during the synthesis of CNTs-CMCs. Five CNT dispersion processes were elucidated with a comparative study of the established research for the homogeneity distribution in the CMCs and the enhanced properties. We also discussed the effect of densification techniques on the properties of CNTs-CMCs. Additionally, we synthesized the outstanding microstructural and functional properties of CNTs in the CNTs-CMCs, namely stimulated ceramic crystallization, high thermal conductivity, bandgap reduction, and improved mechanical toughness. We also addressed the fundamental insights for the future technological maturation and advancement of CNTs-CMCs.

Keywords: ceramic matrix composite; carbon nanotube; CNTs dispersion; densification

1. Introduction

Ceramic materials are well known for their corrosion resistance, chemical inertness, high strength, and high thermal stability, which makes these materials suited for applications involving harsh environmental conditions or high-temperature exposure. Related industries such as metallurgical and chemical sectors demand low-density ceramic materials that possess high refractoriness and corrosion resistance for implementation in the revolutionary application. To meet the demand, numerous ceramic synthesis routes have been established: sol–gel [1,2], supercritical fluid [3,4], hydrothermal [5–7], solid-state [8,9], and polymer-derived ceramics [10,11]. Even with the superior properties and well-established synthesis techniques, monolithic ceramic materials have yet to become the first option applied in bulk structural components, because of the low thermal transport properties, low electrical properties, and brittleness (low fracture toughness K_{IC}). Throughout the years, the scientific and engineering communities have countered the elevated thermal, electrical, and mechanical deficiencies of monolithic ceramics by developing

ceramic matrix composites (CMCs). Many reinforcements (i.e., nanorods, nanotubes, and particulates) have been implemented in bulk glass–ceramics and polycrystalline ceramic matrices. As compared to their counterparts, these reinforced ceramic materials showed significant improvements in their thermal transport and electrical conduction properties, and crack propagation was limited (increasing the strength). The enhanced characteristics allowed CMCs to be engaging materials for structural applications.

In 1991, Iijima from the NEC Corporation (Japan) discovered carbon nanotubes (CNTs) [12], which contribute to many aspects of nanoscience and nanotechnology applications today. CNTs and carbon nanofibers (CNFs, a type of carbon allotrope) share cylindrical shapes, which can be formed by wrapping graphene sheet/s along the axial direction. The difference between CNTs and CNFs is the core structure: a hollow structure for CNTs but a concentric structure for CNFs. Carbon atoms in most types of CNTs are arranged in a honeycomb lattice featuring sp^2 hybridization. CNTs can be commonly found in single-walled carbon nanotubes (SWCNTs, single wrapping graphene sheet) and multi-walled carbon nanotubes (MWCNTs, additional graphene tubes along the core of SWCNTs). The average diameter of pristine SWCNTs is lower than 10 nm and the diameter of pristine MWCNTs ranges from 10 to 100 nm, with both CNT types possessing fullerene capping at the two ends [13]. When it comes to practicability, the main difference between SWCNTs and MWCNTs is the material cost, e.g., 31–1160 USD/gram (SWCNTs) and 11.4–156 USD/gram (MWCNTs), according to Sigma Aldrich. The high cost of SWCNTs is due to the critical environment and parameter control during the fabrication. The preference between SWCNTs and MWCNTs as the ideal filler in the matrix remains debated. Afzal-iTabar et al. reported that the MWCNTs-SiO₂ nanohybrid is a better candidate for Pickering emulsion stability over SWCNTs-SiO₂ [14]. Nadeem et al. compared the Nusselt number (ratio of thermal convection to conduction) of SWCNTs and MWCNTs in water, ethylene glycol, and kerosene, showing that MWCNTs possess lower Nusselt numbers and higher conductive thermal transfer values [15]. Cao et al. reported hexadecyl acrylate with functionalized single carbon nanotubes (HDA-g-SWCNTs) solid–solid phase-change materials as the heat spreader for electronic cooling applications [16]. The reported HDA-g-SWCNTs exhibited a higher electrical conductivity, phase-transition enthalpy, and crystallization enthalpy, but a lower thermal conductivity, than those of HDA-g-MWCNTs.

The nature of CNTs can be crystalline, amorphous, and a mixed state, which depends on the fabrication technique. Several techniques have been reported for CNTs synthesis: arc discharge [12], laser ablation [17], chemical vapor deposition [18], and gas-phase catalytic growth [19]. Arc discharge and laser ablation-synthesized CNTs possess a high-quality graphitic lattice, but high energies are required and the CNTs yield is low. By contrast, chemical vapor deposition (CVD) and gas-phase catalytic growth require relatively low energies but provide CNTs with moderate-quality graphitization. The chirality, geometrical parameters, and synthesis routes are key factors that affect the optical [20], electrical [21], and mechanical [22] properties of CNTs. CNTs also possess remarkable thermal properties such as high thermal stabilities up to 2000 °C [23], and high thermal conductivities ($\kappa_{th} = 600$ W/mK) [24] and thermal diffusivities ($D = 39$ mm²/s) [25].

However, CNTs with such excellent properties are rarely introduced as domains in bulk components; instead, they mostly act as fillers in glass [26], ceramic [27], metal [28], polymer [29] and alloy [30] composites. This is due to the high synthesis cost, the intrinsic toxicity, and the underperformed properties of neat CNTs. The high synthesis cost is a well-known factor causing the CNTs to barely act as a domain structure. From the synthesis routes mentioned, CNTs are produced together with side-products such as amorphous carbon, graphite/graphene layers, and carbon dots. Several steps of purification require extra effort and cost during the chemical and thermal treatment, and they have been made to distinguish CNTs from the carbon impurities and to optimize the CNTs yield. Moreover, the combination of the large surface area and toxicity of CNTs has the potential to be harmful to lungs, modify protein structures, and activate immunological responses [31]; therefore, the composition of CNTs in the domain matrix is controlled in small amounts.

In addition, CNTs as fillers in composites perform better than standalone CNTs. Xiao et al. studied the discharge performance of neat CNTs, VO_2 , and VO_2/CNTs as anodes for lithium-ion batteries [32]. They showed that neat CNTs and bare VO_2 both exhibited low discharge capacities (363.8–177.9 mAh/g), but the VO_2/CNTs composite showed larger capacities ranging from 493 to 301 mAh/g. They reported that the discharge capacity of neat CNTs decreased with the current density from 0 to 400 mA/g, and it remained on a plateau of 260 mAh/g, with the current density ranging from 400 to 2000 mA/g (see Figure 1). The discharge capacity of the VO_2/CNTs -10 mg composite followed a downward trend similar to VO_2 with increasing current density, but with an average of a 41.2% higher discharge capacity. They deduced that the enhancement of the discharge capacity was attributed to the CNTs-induced porosity and larger specific surface area from $13.8 \text{ m}^2/\text{g}$ (VO_2) to $24.8 \text{ m}^2/\text{g}$ (VO_2/CNTs). Peng et al. [33] also found that MWCNTs without the CdS domain showed a near-zero photocatalytic activity for H_2 production under visible light irradiation ($\lambda \geq 420 \text{ nm}$). This was attributed to its semiconductive behavior, which cannot produce H_2 under visible light radiation. With a functionalized MWCNTs content of 10 wt.% (which is optimized), the average H_2 production rate increased from 97.9 (pure CdS) to $174.2 \mu\text{mol}/\text{h}$ (CdS/MWCNTs-10 wt.%). MWCNTs acted as ideal electron acceptors and transfer channels; however, the H_2 production efficiency decreased for CdS containing >10 wt.% MWCNTs. This was due to the relative amount of CdS decreasing with the presence of MWCNTs and the reduction of photogenerated carriers in the photoreaction system.

Figure 1. Comparison of the rate capacities and capacity retention of carbon nanotubes (CNTs), VO_2 , and VO_2/CNTs (Adapted with permission from ref. [32]. Copyright 2018 Elsevier).

After the discovery of CNTs, CNTs-reinforced CMCs (CNTs-CMCs) have gained the attention of researchers for their excellent microwave absorbance [34], water decontamination [35], ceramic strengthening [36], and oxidation and ablation resistances [37]. To ensure the future of CNTs-CMCs, many scientific studies have been conducted, and many have failed. Researchers determined that the remarkable properties of the CNTs-CMCs were the result of how the key challenges along with the CNTs-CMCs processing were eliminated or solved. Generally, the challenges include achieving a homogenous CNTs distribution within the ceramic (see Figure 2), forming a suitable interfacial adhesion, lowering the thermal degradation, and optimizing the sinterability and densification of

the CNTs-CMCs without causing structural damage to the CNTs and ceramic matrix. A previous study revealed an inconsistent improvement in CNTs-CMCs from many aspects, e.g., a CNTs reinforcement of 1 wt.% improved the K_{IC} of CNTs-zirconia by about 9% [38], but the same CNTs content (1 wt.%) strengthened the K_{IC} of CNTs- Al_2O_3 to 36.74% [39]. For microwave application, an identical amount of CNTs addition also showed uncertain performance—the microwave absorption of iron acetylacetonate-modified polymethylsilsesquioxane polymer-derived ceramic composites, PMS(Fe), containing 3% of MWCNTs improved by 29% [34], while 3% of CNTs- $Sc_2Si_2O_7$ reached a 175% absorption [40], as compared to their counterpart. The role of the CNTs reinforcement mechanism has yet to be elucidated and established for high amounts of CNTs contained in the CNTs-CMCs. To explain the enhancement of properties of CNTs-CMCs, the mechanism and possible deformation at low-dimensional scales and subsequent postulated formulations need to be investigated.

Figure 2. The illustration of (a) sintered ceramic matrix composite (CMC) and (b) sintered carbon nanotubes reinforced ceramic matrix composite (CNTs-CMC). As compared to bare CMC, the CNTs-CMC grains are tailored through CNTs bridging (the black lines in (b)). Homogenous CNT dispersion and bridging (interfacial adhesion) restricted the crack propagation and improved the fracture toughness of CNTs-CMC.

Therefore, the present review contains four sections, comprehending the overall knowledge of the CNTs-CMCs processing-densification-property correlations. Section 2 introduces the critical challenges during the CNTs-CMCs fabrication and the end product characteristics. Section 3 discusses various processing methods for the dispersion of CNTs into the ceramic matrix to distinguish the processing's complexity and efficacy. Section 4 contributes to a thorough review of established CNTs-CMCs densification and sintering techniques and the effects on the characteristics of the end product. Finally, the functional properties of CNTs-CMCs are highlighted in Section 5. The simple advantage-disadvantage comparison on the CNTs-CMCs processing and densification and sintering routes are displayed, concluded, and summarized.

2. Critical Challenges

2.1. Homogenous Dispersion

This is the most difficult challenge when preparing CNTs-CMCs. The nanotubes are most likely bundled or agglomerated, and this causes a non-uniform distribution within the composites. A non-uniform CNTs distribution will lead to the degradation of the fracture toughness upon indentation analysis. A large amount of CNT bundles cause porosity and reduce the contribution of CNTs to the reinforcement mechanism [41]. It also impacts the

anisotropic properties of ceramics [42], and it results in a significant difference in radial cracks perpendicular and parallel to the random CNTs orientation where the degree of CNTs bridging is low [43]. Various dispersion methods have been developed to disperse CNTs homogeneously and eventually enhance the CNTs-CMCs properties. Sol-gel [44], hydrothermal/solvothermal [45], and colloidal processing [46] are examples of applications of surface functionalization on CNTs to achieve a homogeneous dispersion, while the in situ growth of CNTs by chemical vapor deposition (CVD) can achieve a homogeneous CNTs distribution via growing CNTs at the designed growth site (the metal catalyst) within the ceramic precursor [47].

2.2. Suitable Interfacial Adhesion between CNTs and Ceramic

Functional properties such as thermal and mechanical properties are highly dependent on the interfacial adhesion and the surface morphology [29]. For instance, strong phonon scattering takes place when there is a weak CNTs–ceramic interaction, resulting in a large thermal resistance. Moreover, a weak CNTs–ceramic interfacial adhesion enhances the crack propagation and negatively influences other toughening mechanisms such as crack bridging [48–50]. CNTs with a large lattice oxygen content will deteriorate mechanical properties such as surface hardness and wear depth, where the surfaces between CNTs and the domain ceramic are incompatible and the adhesion is extremely weak [43,51]. A high chemical inertness of pristine CNTs is the major cause of the near-zero chemical affinity of CNTs toward the ceramics. CNTs are neither polar nor lipophilic and ordinary aromatic, where the π -electron population is not balanced by the aromatic hydrogens.

Surface functionalization helps to enhance the quality of CNTs adhesion and increase the chemical affinity toward the matrix. During the functionalization, the CNT walls are partially damaged and attached with functional groups such as carboxyl (–COOH) [41], hydroxyl (–OH) [52], amine (–NH₂) [53] groups, and C–F [54] bonds. The attached functional groups provide hydrophilic properties to CNTs for a stable water (or solvent) dispersion [55] and also to improve the interfacial adhesion with the ceramic matrix, which expresses the enhancement in terms of K_{IC} [56], Young's modulus [57], corrosion resistance [58], and thermal conductivity [59]. Hence, the interface engineering is essential to understand and overcome the development of extremely hard, strong, and low-density CNTs-CMCs.

2.3. Thermal Degradation

During the densification and sintering of CNTs-CMCs, the temperature, pressure, environment, and duration are important for the crystallization of the ceramic and the maintaining of the primitive nature of CNTs. Studies in the literature have shown that high pressures, high sintering temperatures, and prolonged sintering durations can negatively affect the CNTs' nature and cause allotropic transformation and thermophysical damage [60]. Structural damage on the CNT walls was observed in CNTs-CMCs when they underwent spark plasma sintering (high temperature and pressure) and pressureless sintering (long sintering duration) [61].

3. Processing Methods

3.1. Powder

Powder processing is an established CNTs-CMCs fabrication technique for the production of near-net shape products. This technique is also useful for its batch production and the integrated weight fractions of the raw material. Powder processing requires two or three steps. Figure 3 compares the two-step and three-step powder processing. The two-step powder processing involves the mixing of CNTs and ceramic powder, followed by in situ densification and sintering such as spark plasma sintering (SPS) and hot-press sintering (HPS), while the three-step processing involves mixing, densification, and sintering, such as pressureless sintering (PLS) and microwave-assisted sintering (MAS). Several techniques could be applied at the mixing process: manual mixing [62], planetary milling [63],

ball milling [38,64,65], and high-energy ball milling [66]. The mixing is commonly performed using dry CNTs and ceramic powder, but it often requires a solvent like alcohol or acetone as a medium, known as wet-mixing, where the solvent is later evaporated. Removing the aggregation and achieving a homogenous CNTs distribution are the ultimate goals of this step. This processing technique is suitable for preparing CMCs with large amounts of CNTs, and it is applicable to the thermal enhancement [62,67] and mechanical enhancement [68,69] of CNTs-CMCs.

Figure 3. Conceptual setup for (a) the two-step and (b) the three-step powder processing methods.

Ye et al., improved the K_{IC} and flexural strength of barium aluminosilicate (BAS) glass–ceramic composites by adding MWCNTs through wet powder processing [70]. They sonicated and ball-milled the MWCNTs-BAS in ethanol into the MWCNTs-BAS slurry. Next, the slurry was dried and hot-pressed (1600 °C, 1 h, 20 MPa, N_2 atmosphere) into ceramic pellets for mechanical analysis. They noticed that the addition of 10 vol.% MWCNTs increased the flexural strength from 84 to 245 MPa (about 300%) and the K_{IC} increased from 1.22 to 2.97 $MPa \cdot m^{1/2}$. Good MWCNTs-BAS interfacial bonding, the high elastic modulus of CNTs, and the CNTs bridging contributed to the enhanced mechanical properties. By contrast, the relative density of 15 vol.% CNTs-added composites decreased by 3% and the flexural strength only achieved 169 MPa, which was due to the effect of the agglomerated CNTs (see Figure 4). Moreover, Chan et al. reduced the lattice strain of zinc silicate CMCs upon the addition of CNTs [71]. They prepared CNTs through CVD on a cobalt oxide metal catalyst and through the manual mixing of the CNTs with zinc silicate glass powder. The CNTs-zinc silicate glass powder was further sintered in Ar atmosphere, and the zinc-silicate glassy phase changed to the polycrystalline willemite phase (Zn_2SiO_4). Through the phase analysis, CNTs showed an insignificant phase alteration to the domain Zn_2SiO_4 crystal structure but only introduced the graphite (C) and cobalt oxide (CoO) phases. They also noticed that the lattice strain of 3 wt.% CNTs- Zn_2SiO_4 reduced by 22.85% and the crystallite size of 1 wt.% CNTs- Zn_2SiO_4 CMC increased by 5.65%, as compared to the CNTs-free Zn_2SiO_4 composite.

Figure 4. (a,b) Scanning electron microscope (SEM) micrograph of 10 vol.% CNTs-BAS composite upon indentation. The white arrows indicate the bridging effect of CNTs during the indentation crack propagation. (b) The enlarged micrograph from the white square section in (a), showing the CNTs pullout from the barium aluminosilicate (BAS) composite. (c,d) The flexural strength and fracture toughness peaked at the addition of 10 vol.% CNTs, which indirectly indicates that the practicable CNTs addition in the BAS composite is 10 vol.%. (Adapted with permission from ref. [70]. Copyright 2006 Elsevier).

3.2. Colloidal

Colloidal processing involves several physical/chemical practices to disperse CNTs with water/solvent, eventually turning into CNT nanofluid. The options of the CNT dispersant are limited because it needs to meet the dispersion compatibility and the sinterability upon the densification and sintering with the ceramic domain. Critical dispersion steps, such as sonication, magnetic stirring, and chemical oxidation, are taken for the CNTs nanofluid production. The CNT nanofluid is added to the ceramic powder and densified for the final CNTs-CMCs product. Figure 5 displays the schematic of colloidal processing.

Figure 5. Schematic diagram of colloidal processing. (a) Dispersing CNTs into CNT nanofluid and (b) ceramic powder mixed with CNT nanofluid, which dried out the moisture, densified and sintered into CNTs-CMCs pellets.

N,N-Dimethylformamide (DMF) was first applied to disperse the low concentration of MWCNTs and SWCNTs with near-zero disruption to the structure [72]. Acetone was applied onto oxidized MWCNTs to achieve dispersion where acetone formed the solubilizing phase with the hydroxylated modified MWCNTs surface [73]. Carboxylated MWCNTs (MWCNTs-COOH) can be dispersed in diethyl ether with the addition of 4-fluoroaniline in a N_2 atmosphere [54]. Molecular dynamic (MD) simulations [74] and experimental studies [75] showed that pyrogallol and 1-naphthol had high binding coefficients to MWCNTs and increased threefold as the experimented MWCNTs diameter reduced from 100 to 10 nm (effect of agglomeration increased as diameter decreased). Solvents with a high density of aromatic structure are mostly dispersed SWCNTs at ease with the aid of planar polycyclic aromatic hydrocarbons as compared to linear structure solvents [76]. Previous studies in the literature on the dispersion medium, surfactant, and other additives are displayed in Table 1.

Table 1. Dispersion medium and additive added to multi-walled carbon nanotube (MWCNT) nanofluid.

Dispersion Medium	Additive/Surfactant	Outcome *	Reference
Distilled water	Polyethyleneimine (PEI)	High-stability CNTs nanofluid CNTs-Al ₂ O ₃ H _V : 16.9–17.6 GPa K _{IC} : 3.7–4.9 MPa	[77]
Ethanol	n/a	CNTs-Al ₂ O ₃ Electrical conductivity: 4.5×10^{-15} to 6.2×10^{-2} S/m K _{IC} : 3.78–4.66 MPa·m ^{1/2} Strength: 334–390 MPa	[78]
CTAB for CNTs and PAA for SiO ₂	n/a	CNTs-SiO ₂ ceramic 97% relative density (ρ %)	[79]
Distilled water	chitosan	Non-Newtonian shear-thinning fluid κ_{th} : +13% with 3 wt.% CNT	[80]
Distilled water	Polyvinyl pyrrolidone (PVP)	κ_{th} : +22.2% (0.5 wt.% CNTs and 0.01 wt.% PVP in water)	[81]
Water	n/a	κ_{th} : +24.8% (1 wt.% CNT)	[82]
Denatured alcohol (85% ethanol and 14% methanol)	n/a	CNTs nanofluid with solar absorption near 100%.	[83]
Distilled water	Arabic gum	0.085 wt.% CNT κ_{th} : +67–250% for temperature range of 25–55 °C	[84]
Deionized water	Xanthan gum (XG)	0.1 wt.% CNTs: 0.2 wt.% XG: water κ_{th} : 0.65–0.76 W/mK at 70 °C	[85]
Deionized water	Triton X-100 Pluronic F-127 Sodium dodecyl sulphate (SDS) CTAB	Stability in the aspect of inertial cavitation activity CNTs-SDS lowest stability	[86]
Isopropyl alcohol (IPA)	Polyvinyl alcohol (PVA)	CNTs-MgB ₂ superconductor J _C : 10 ⁴ A/cm ² at 3.5 T and 20 K 10 times higher than that of the pure sample	[46]
Deionized water	Potassium persulfate (K ₂ S ₂ O ₈)	CNT nanofluid 1.2 vol.% CNTs at 3.4 thermal transfer performance	[87]
Distilled water	Toluidine blue (C ₁₅ H ₁₆ ClN ₃ S)	CNTs-Mn ₃ O ₄ Enhanced supercapacitance	[88]

* K_{IC}: fracture toughness; κ_{th} : thermal conductivity; J_C: critical current density.

3.3. Sol–Gel

Sol–gel processing techniques are effective for fabricating CNTs-CMCs with a homogenous CNT dispersion and a uniform size distribution of ceramic crystals. CNTs are sonicated in an aqueous solution (or solvent) with minimum surfactant addition (known as the CNT sol). In order to prepare CNTs-CMCs gel, a series of solutions (ceramic precursor, gelling agent, and pH control agent) are added into the CNT sol, and ageing or the gelation process is carried out. The CNTs-ceramic gel is then dried, calcined at high temperature with (without) inert gas, and left with the CNTs-ceramic powder (see Figure 6).

Figure 6. Schematic diagram of CNTs-CMCs sol-gel processing.

Liu et al. compounded strontium titanate (SrTiO_3)-coated MWCNTs in epoxy resin (EP) toward high-dielectric-constant percolative polymer composites [89]. First, they prepared an Sr^{2+} aqueous solution and TiO_3^{2-} ethanol solution, with acetyl acetone as the chelating agent. Then, they added the acidified MWCNTs with sodium dodecyl benzene sulfonate (SDBS) as the CNT surfactant into the as-prepared SrTiO_3 solution. The SrTiO_3 -MWCNTs composites were stirred for 3 h at 40 °C (gelation), dried overnight, and calcined at 800 °C before compounding with EP. The obtained dielectric constant of EP-compounded 11 vol.% SrTiO_3 -MWCNTs reached 283 and the dielectric loss was 0.07 at 1 kHz, where the dielectric constant of EP-compounded 11 vol.% neat MWCNTs reached 1600 and the dielectric loss was 25. They deduced that the SrTiO_3 coating acted as barriers between CNTs, and it resulted in a low dielectric loss, which improved the dielectric properties. The tribological properties of the metal/alloy surface can also be enhanced when it is coated with a thin layer of CNTs-CMCs. Xu et al. coated a 0.25 wt.% CNTs- Al_2O_3 - ZrO_2 - ZrSiO_4 ceramic sol-gel mixture on A4 steel to enhance the wear rate at an escalated temperature [90]. Acidified CNTs were first dispersed in SDBS solution, transferred to the aluminium dihydrogen phosphate $\text{Al}(\text{PO}_2(\text{OH})_2)_3$ solution (containing the ceramic powder), and cured for 5 h before brushing on the steel surface. It showed that the CNT fillers (0.25 wt.%) effectively lowered the CNTs-CMCs-coated steel's wear rate with temperature: 57% (100 °C), 67% (300 °C), and 87.5% (500 °C), as compared to the bare ceramic coating.

Moreover, sol-gel processing is a favourable technique during the carbon-ceramic electrode (CCE) fabrication for its high CNT dispersion homogeneity. CNTs incorporating CCE were developed to detect nicotinamide adenine dinucleotide (NADH) [91], sulfonamide drugs [92], and purine derivative [93], as well as for wastewater treatment [94]. Ferrag et al. developed CNTs-Au-CCEs to detect the purine derivatives, uric acid (UA), xanthine (XA), and caffeine (CA) [93]. They mixed 3-mercaptopropyl-methyl-dimethoxy silane (MPDS, Si-based sol-gel network), hydrochloric acid, and the carbon mixture (50 mg CNTs: 150 mg graphite powder) in methanol, and they dried out the liquid mixture. The dried ceramic product was impregnated with Au solution and then molded in a narrow glass tube. Comparing the CNTs-Au-CCEs and the bare CCE, the diffusion coefficients for UA, XA, and CA improved: 3.5 times (UA), 1.56 times (XA), and 2.26 times (CA). The limit of detection (LOD) values of the CNTs-Au-CCE for UA, XA, and CA were 50, 63, and 354 nM, where the limits of quantification (LOQ) were 167, 209, and 1179 nM, respectively. Table 2 shows the dispersion medium, dispersant (or surfactant), gelling agent, and the gelation process when preparing the CNTs-CMCs gel.

Table 2. The dispersion medium and dispersant of CNT sol, and the CNTs-CMCs gelling agent and gelation process.

Dispersion Medium for CNT Sol	Surfactant/Dispersant for CNT Sol	Gelling Agent	Gelation or Aging Process (after Adding Ceramic Sol)	Reference
Ethanol	-	-	Dried overnight	[95]
Dimethyl formamide (DMF)	-	Ammonia (NH ₃)	Aging 80 °C, 2 h	[96]
Butanol	PVP	Benzen-1,4-diol ^a	Heat 105–115 °C, 2.5 h	[97]
Water	-	Nano silica sol–gel	Stirred 1 min, molded, and cured at 20 °C	[98]
Water	SDBS	Acetyl acetone ^b	Stir 40 °C, 3 h	[89]
Water	Ammonium stearate ^c	Acetyl acetone	Stir 30 min, ambient	[99]
Water	-	NH ₃	Stir 3 h and age for 24 h	[100]
Water	SDBS ^d	Acetyl acetone	Stir 40 °C, 2 h	[101]
Boehmite sol (AlOOH)		NH ₃	In situ gelation (1–2 min)	[44]
Water	SDBS	Aluminium dihydrogen phosphate solution ^e	Curing 5 h with temperature 50–270 °C	[58,90]

^a HOC₆H₄OH. ^b CH₃C(O)H=C(OH)CH₃. ^c CH₃(CH₂)₁₆COO[−]NH₄⁺. ^d Sodium dodecylbenzene sulfonate CH₃(CH₂)₁₁C₆H₄SO₃[−]Na⁺. ^e Al(PO₂(OH)₂)₃ solution.

3.4. In Situ CNTs Growth

In situ synthesis is the attempt for CNTs-CMCs to grow CNTs on the ceramic matrix directly, and it is widely performed through chemical vapour deposition (CVD). Generally, the ceramic powder is prepared with metal salt (such as metal nitrate or acetate salt) in an aqueous solution or solvent to ensure complete metal ion impregnation within the ceramic domain. Next, the ceramic-metal solution is reduced at high temperature with the presence of H₂ as the metal salt reduces to metal oxides and further reduces to metal nanoparticles. The nanoparticles act as the active growth site for CNTs, so the carbon solubility is critical. The commonly used transition metal catalysts are Fe, Ni, and Co for their moderate-to-high carbon solubility at elevated temperatures. Carbon atoms for the CNTs growth come from the carbon precursor (CH₄, C₂H₂, ethanol, etc.) and are carried by the flowing gas (such as Ar, N₂, He) within the CVD system (see Figure 7). The deposition of carbon atoms (carbonaceous molecule from the carbon precursor) involves several mechanisms: carbon adsorption on the catalyst surface, the dissolution of carbon molecules (segregation of hydrogen bonding), carbon diffusion into the catalyst, the formation of the carbon network and the growth of CNTs. Table 3 displays the optimum parameters for in situ CNTs growth on ceramic.

Figure 7. In situ processing of CNTs-CMCs by thermal chemical vapour deposition (CVD).

Chen and co-workers prepared Si_3N_4 -CNTs composites through in-situ CNTs growth via CVD [102]. The ceramic possessed an extraordinary electromagnetic shielding effect over the X-band frequencies ($f = 8.2\text{--}12.4\text{ GHz}$), where the total shielding effectiveness increased from 6.0 (neat Si_3N_4) to 30.4 dB (2.7 wt.% CNT). They impregnated Si_3N_4 with 10 wt.% cobalt acetate tetrahydrate ($\text{CoAc}\cdot 4\text{H}_2\text{O}$) and fed the CVD system with Ar-carried acetone vapor $(\text{CH}_3)_2\text{CO}$. Vapor deposition took place at $550\text{ }^\circ\text{C}$ and lasted for 1 h. As per 10 wt.% CoAc catalyst, they managed to produce 2.7 wt.% feather-like CNTs (outer diameter, $d = 10\text{ nm}$) with a $0.75\text{ }I_D/I_G$ ratio (see Figure 8). The growth of CNTs interconnected the Si_3N_4 grains and improved the shielding properties. The resulting Si_3N_4 -2.7 wt.% CNTs composites improved the absorbance shielding effectiveness (SE_A) from >5 (neat) to 22 dB, and the reflectance shielding effectiveness (SE_R) increased from 2 to 8 dB over the X-band.

Figure 8. Scanning electron microscope (SEM) images and fracture surface images of (a) neat Si_3N_4 , (b) 2 wt.% CoAc, (c) 4 wt.% CoAc, and (d) 10 wt.% CoAc. The resulting CNTs contents are 0, 1.49, 1.97, and 2.70 wt.%, respectively. (Adapted with permission from ref. [102]. Copyright 2015 Elsevier.)

To improve the Cu^{2+} removal of the porous Al_2O_3 ceramic membrane, Tofighy and Mohammadi grew CNTs on the membrane by using an organometallic catalyst (Ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$) and cyclohexanol $\text{HOCH}(\text{CH}_2)_5$ as carbon feedstock [103]. Under transmission electron microscope (TEM) observation, the outer diameter of CNTs ranged from 30 to 40 nm, and it showed a rigid and flawless structure. The Al_2O_3 -CNTs membrane was tested for the permeation flux and rejection of Cu^{2+} ions in a weak acidic environment ($\text{pH} = 6$) for 10 min. The permeation flux reduced from 523.65 to 45.98 $\text{kg}/\text{m}^2\text{h}$, while the Cu^{2+} rejection increased from 2.76% to 20.27%. They discussed that the reduced permeation flux and the increased Cu^{2+} rejection were the outcomes of the CNTs filling the membrane pore void, as it increased the membrane resistance. Ding et al. grew CNTs

on FeCl₃-implanted polysiloxane at 800–1500 °C for high electromagnetic waves (EMW)-absorbing applications [104]. Instead of using gas-carried precursor vapor, they dissolved the FeCl₃-polysiloxane in ethanol and carried out the reaction for 2 h in Ar atmosphere. During the CVD at 900 °C, the I_D/I_G ratio was 1.01, and the measured CNTs crystallite size (L_a, Equation (1), where λ is the laser wavelength of the Raman spectroscopy) [105,106] was 16.65 nm. However, more defects formed on the CNTs, causing the I_D/I_G ratio to increase to 2.46 and L_a to decrease to 6.84 nm when the reaction temperature was 1500 °C. Transmission electron microscope (TEM) analysis revealed that the CNTs experienced a structure breakdown, and the SiC grew in various morphologies such as microspheres, needle-like, and nanowires at high temperature. In this case, CNTs provide a casting mold for the growth of SiC micro- and nanostructures, and the formed SiC showed a low reflection loss of −58.37 dB at 10.11 GHz.

$$L_a(\text{nm}) = (2.4 \times 10^{-10}) \lambda^4 \left(\frac{I_D}{I_G} \right)^{-1} \quad (1)$$

Table 3. The optimum CVD parameters for in situ CNTs growth on CMCs.

Catalyst/CNTs Growth Site	Precursor	Deposition Atmosphere	Deposition Temperature and Duration	Reference
Cobalt Acetate tetrahydrate CoAc·4H ₂ O	Acetone (CH ₃) ₂ CO	Ar	550 °C, 60 min	[102]
Ferrocene Fe(C ₅ H ₅) ₂	Cyclohexanol HOCH(CH ₂) ₅	400 sccm N ₂	750 °C, 60 min	[103]
Iron (III) chloride FeCl ₃	Ethanol C ₂ H ₅ OH	Ar	800–1500 °C, 120 min	[104]
Iron (II) chloride tetrahydrate FeCl ₂ ·4H ₂ O	Acetylene C ₂ H ₂ (10 sccm)	500 sccm N ₂	700 °C, 120 min	[107]
Nickel nitrate hexahydrate Ni(NO ₃) ₂ ·6H ₂ O	Methane CH ₄ (150 sccm)	300 sccm N ₂	1000 °C, 120 min	[47]
Iron (III) nitrate nonahydrate Fe(NO ₃) ₃ ·9H ₂ O	Methane CH ₄ (100 sccm)	n/a	800 °C, 150 min	[108]
Ni(NO ₃) ₂	Ethylene C ₂ H ₄	H ₂	700 °C, 20 min	[40]

In situ synthesis is a simple method to synthesis large volumes of CNTs-embedded CNTs-CMCs with a minimum amount of bundled CNTs and agglomeration. Besides, this method provides CNTs-CMCs with a highly ordered unidirectional orientation, which is enables the comparison of the toughening mechanism between microfibers-reinforced ceramic and CNTs-CMCs. However, the quality of CNTs within the ceramic is not consistent, because the CNTs growth mechanism on the active metal nanoparticles is greatly dependent on various parameters—temperature, deposition duration, amount and purity of metal catalyst, gas flow, and carbon precursor.

3.5. Hydrothermal/Solvothermal Processes

Hydrothermal and solvothermal processes are well-established CNTs-CMCs techniques for homogenous CNT dispersions with a low number of impurities. Generally, acid-functionalized CNTs are dispersed in water (hydrothermal) or solvent (solvothermal), together with the ceramic salt with (without) the surfactant. The surfactant reduces the interfacial resistance among the ceramic salt, CNTs, and the dispersion medium. The aqueous mixture of CNTs and salt is magnetically stirred or sonicated for CNTs disentanglement and to improve the CNTs-CMCs homogeneity. Next, the mixture is stored in an autoclave

and heated from 100 to 250 °C for several hours to several days, highly dependent on the crystallization of the domain ceramic (Figure 9).

Figure 9. Hydrothermal (or solvothermal) processing scheme of CNTs-CMCs.

Zhao et al. prepared low-bandgap MWCNTs-Bi₂S₃ composites for methylene blue (MB) wastewater treatment [109]. Before the hydrothermal processing, they applied acid treatment (stirred with HNO₃, 80 °C, 12 h) to functionalize CNTs. The CNT wall with the carboxyl group -COOH resulted in a higher miscibility with water. The composite was prepared by stirring the bismuth nitrate (Bi(NO₃)₃·5H₂O), urea, and MWCNTs in deionized water and heating in an autoclave at 120 °C for 12 h. The hydrothermally treated composites were centrifuged, rinsed with alcohol-water, and dried overnight into MWCNTs-Bi₂S₃ ceramic powder. Using 5 wt.% MWCNTs, the bandgap value of Bi₂S₃ powder reduced from 1.245 to 0.875 eV, and the Brunauer–Emmett–Teller (BET) surface area increased from 35.2 to 36.1 m²/g. With the low-bandgap value and larger surface area, the photocatalytic activity (the MB degradation) under visible-light irradiation reached 90.75% in the first cycle and was maintained at about 75% after the fourth cycle. Besides, MWCNTs as the filler effectively improved the sensing device, e.g., ammonia sensor. Singh et al. shortened the response and recovery time of a MoS₂-based ammonia sensor by adding a relatively low amount of CNTs during the hydrothermal process [45]. They prepared the ceramic ammonia sensor by sonicating 1 g of ammonium tetra-thiomolybdate (NH₄)₂MoS₄, 10 mL of hydrazine monohydrate N₂H₄·H₂O, and 3 mg of MWCNTs in deionized water. Next, the mixture was transferred to an autoclave, heated at 200 °C for 12 h, and dried in an oven for 2 h. The obtained black powder (after drying) showed a larger surface area of 20.23 m²/g, where the surface area of neat MoS₂ was 4.22 m²/g. For the ammonia response determination, neat MoS₂ required 400 s to detect the NH₃ content when the concentration was low as 150 ppm, while the MoS₂-MWCNTs hybrid was more capable of rapid detection (response time = 65 s), which was six times faster than the neat one and was due to the larger surface area. Li et al. discussed the dielectric performance of the poly(1-butene) polymer filled with modified polydopamine and Ba(Zr_{0.2}Ti_{0.8})O₃-MWCNTs as a diaphragm in capacitors [110]. The Ba(Zr_{0.2}Ti_{0.8})O₃-MWCNTs were prepared through sol–gel processing on barium acetate Ba(COOCH₃)₂ (dissolved in acetic acid and DI) and tetrabutyl titanate Ti(CH₃(CH₂)₃OH)₄ (dissolved with isopropanol zirconium in glycol methyl ether), and then by carrying out the hydrothermal processing with MWCNTs in NaOH aqueous solution. The temperature and duration of the hydrothermal process was set at 180 °C for 24 h, and the obtained Ba(Zr_{0.2}Ti_{0.8})O₃-MWCNTs was then transferred on the poly(1-butene) polymer film. The analysis showed that the dielectric constant of the film improved from 4.4 to 28.40 with the addition of 0.5 vol.% CNTs at 1 kHz, and the dielectric loss was 0.0077, which makes this composite a potential candidate as an intermediate phase and insulating layer.

In addition to hydrothermal treatment, solvothermal processing also offers promising results. Vadivel et al., improved the BiPO₄ nanorod's capacitance and its photocatalytic activity on methyl orange degradation by introducing MWCNTs via the solvothermal process [111]. They dispersed bismuth nitrate (Bi(NO₃)₃, Bi³⁺ precursor), monoammonium phosphate (NH₄H₂PO₄, PO₄^{3−} precursor), and untreated MWCNTs (with PVP as a surfactant) in ethylene glycol (EG). The weight ratio of the mixture Bi³⁺:PO₄^{3−}:MWCNTs was 1.5:0.85:0.05. The mixture was then sealed in an autoclave and heated at 160 °C for 12 h. The measured specific capacitances (current density = 1 A/g) of neat MWCNTs and pristine BiPO₄ were 45 and 292 F/g, respectively, while the BiPO₄-MWCNTs reached 368 F/g at the identical current density. The stable photocatalytic activity of the composite under indigo irradiation (464 nm) also reached 95% of methyl orange degradation after a 150 min test time. The enhanced capacitance and photocatalytic activities were due to the large surface area of BiPO₄-MWCNTs (38.25 m²/g), which was 1.53 times larger than that of pristine BiPO₄. Solvothermal processing also enables the oxide coating on the wall of CNTs. Zhang and Hao coated layers of rare earth oxide on the CNTs wall toward the effective thermal decomposition of ammonium perchlorate (AP, a type of oxidizer in solid propellant) [112]. They enlarged the surface area of CNTs with HNO₃, and they modified the CNTs polarity with cetyl trimethylammonium bromide (CTAB) and poly(sodium 4-styrenesulfonate) (PSS). The rare earth nitrate salt (Y³⁺, Nd³⁺, and Sm³⁺), modified CNT, sodium acetate (NaAc), and polyethylene glycol (PEG) were dissolved and stirred in EG, and they were heated in the reaction system in a 200 °C oil bath for 2.5 h. The AP's thermal decomposition peak temperature reduced from 452 to 326.5 °C with the addition of 2 wt.% Y₂O₃-CNTs, and the DTA heat released increased from 0.281 to 2.308 kJ/g. It showed that the thermal decomposition of AP decreased because of the large surface area and the partially filled 4d orbital in the rare earth material, which is favorable for electron transfer. Tables 4 and 5 show the optimized parameters of the surfactant-CNTs ratio and the hydrothermal (solvothermal) processing.

Table 4. Optimized dispersion agent and autoclave heating parameters of hydrothermal processing.

CNTs Type and Treatment	Dispersion Agent and the Mass Ratio (Dispersion Agent: CNTs)	Autoclave Heating Temperature (°C)	Autoclave Heating Duration (h)	Reference
HNO ₃ -treated MWCNTs	-	210	24	[113]
Untreated MWCNTs	Glycolic acid (0.857:0.129)	200	2	[114]
HNO ₃ -treated MWCNTs	-	120	12	[109]
Untreated SWCNTs	-	180	8	[61]
Untreated MWCNTs	Hydrazine monohydrate ^a (10 mL:3 mg)	200	12	[45]
Untreated MWCNTs	NaOH	180	24	[110]

^a N₂H₄·H₂O.

Table 5. Optimized dispersion agent and autoclave heating parameters of solvothermal processing.

Dispersion Medium	Dispersion Agent and the Mass Ratio (Dispersion Agent: CNT)	Autoclave Heating Temperature (°C)	Autoclave Heating Duration (h)	Reference
Ethanol + water	-	180	24	[115]
Ethylene glycol (EG)	PVP (0.75:0.05)	160	12	[111]
EG	PEG (1:0.03)	200	2.5	[112]
EG	-	180	3	[32]

Hydrothermal and solvothermal processes bring benefits in preparing high-quality CNTs-CMCs with low synthesis temperatures. However, the processing duration (involving heating, cooling, and drying) is longer than those of other processing techniques. In addition, the starting materials such as the ceramic precursor and the surfactants (or dispersants) for CNT dispersion are expensive, and the final yield is low because the molecular ratio of ceramics in the precursor is mostly low. For example, the stable hydrogen evolution reaction (HER) candidate, molybdenum sulfide/reduced graphene oxide-carbon nanotube composites ($\text{MoS}_2/\text{RGO}/\text{CNTs}$), was where the MoS_2 compound was produced from ammonium thiomolybdate salt $(\text{NH}_4)_2\text{MoS}_4$ [113]. The weight ratio of one mole of MoS_2 is about 61% per one mole of the $(\text{NH}_4)_2\text{MoS}_4$. A small amount of end product explains that the hydrothermal and solvothermal processes are not favorable in CNTs-CMCs mass production, but they are fit for research purposes and the high-purity requirement.

4. Densification and Sintering Techniques

Densification and sintering are the critical treatments for CNTs-CMCs interaction by shaping the powder and supplying energy (thermal/electrical) to the matrix itself. This process inputs high energy in promoting the crystallization of the domain ceramic crystal and bond-breaking of $\text{C}=\text{C}$ bonds of CNTs. Generally, a CNTs-CMCs pellet with a desired dimension is produced through an applied pressure before or during the thermal treatment. Hereafter, four common techniques are reviewed: spark plasma sintering (SPS), hot-press sintering (HPS), pressureless sintering (PLS), and microwave-assisted sintering (MAS). The rapid heating in SPS and MAS offers a time-efficient route by heating the CNTs-CMCs at a high temperature for a short duration (<15 min); however, the setup and fabrication are expensive. On the other hand, HPS and PLS produced a cheaper composite with flexible size and shape, yet at the risk of a lower density and long sintering duration (>1 h).

4.1. Spark Plasma Sintering (SPS)

The success of spark plasma sintering (SPS) has been highlighted by noteworthy achievements of, for example, an outstanding increase in tensile strength of ceramic material composed of CNTs. During the SPS process, the CNTs-ceramic mixed powder is sintered under the simultaneous effect of a pulsed direct current (PDC) and an applied pressure in a vacuum chamber. The powder is placed in a die, pellet-pressed by the plunger, and current-heated by passing a DC [116] through the die and the sample (see Figure 10). The heating rate, the application of pressure, and the current are the three main parameters in determining the microstructural and mechanical properties of the sintered pellet.

Figure 10. Spark plasma sintering (SPS) schematic setup.

Zhan et al., was the first to perform the SPS process on a CNTs-ceramic composite. They fabricated a SWCNTs-aluminum oxide composite with an applied pressure of 63 MPa and a high-temperature plasma of 1150 °C in a 3 min sintering period. It was noticeable that the electrical conductivity increased from 1×10^{-12} to 1050 S/m and the fracture toughness, K_{IC} , increased from 3.3 to 9.7 MPa·m^{1/2} [117,118]. These pioneer works had inspired the present researchers in using the SPS process to fabricate CNTs-ceramic composites. Recently, homogenization was first applied to avoid the aggregation of CNTs during the SPS process. Lamnini et al. applied 5 h high-efficiency attrition milling at 4000 rpm on the MWCNTs-8YSZ (8 vol.% yttria-stabilized zirconia) powder, and they applied SPS to the powder to form pellets at 1400 °C with a 50 MPa plunging pressure for 5 min. The enhanced K_{IC} of the MWCNTs-8YSZ composites (3.2 MPa·m^{1/2}) was attributed to the MWCNTs crack deflection and crack bridging between ceramic particles [38]. Momohjimoh et al. compared MWCNTs and SiC as dopants in the alumina matrix for electrical conductivity performance. After performing 50 MPa and >1400 °C sintering on the composites, 2 wt.% MWCNTs-alumina achieved a low-density ceramic matrix with a high electrical conductivity of 101.118 S/m [119]. Table 6 shows the reported research on fabricating CNTs-CMCs through SPS technique.

Table 6. Previous work on CNTs-CMCs composite via SPS technique.

Raw Material	Dispersion Procedure	SPS Parameter	Outcome *	Reference
TiO ₂ , amorphous boron, MWCNTs	Sonication in toluene	1400 °C, 50 MPa, 10 min	6 vol.% CNTs-TiB ₂ -TiC composites CTE: −10.64% Grain size reduced 92.93%	[120]
SiC, amorphous boron, MWCNTs	Planetary mill	2000 °C, 50 MPa, 5 min	1 wt.% CNTs-SiC-B Porosity: −55.56% Density: +3.32%	[121]
TiN, MWCNTs	Sonication in ethanol	1900 °C, 40 MPa, 7 min	5 wt.% CNTs-TiN Density: −6.13%	[122]
CaCO ₃ , CuO, TiO ₂ , MWCNTs	High-energy-vibration ball mill	1000 °C, 50 MPa, 5 min	18 wt.% CNTs-CaCu ₃ Ti ₄ O ₁₂ Negative permittivity behaviour	[123]

* CTE: coefficient of thermal expansion; HEBM: high-energy ball milling; TiN: titanium nitride/tinite.

4.2. Hot-Press Sintering (HPS)

Pressure-assisted sintering/hot-press sintering is the “in situ temperature and pressure sintering” technique, which turns CNTs-CMCs powder into pellets or films. The schematic setup is shown in Figure 11. The graphite dies, inside a vacuum chamber, hold the mixed powder. The mixed powder is pressed to several MPa and heated up for several hours. This technique is suitable for ceramics that need extreme-condition fabrication. Through pressure-assisted sintering, the thermo-physical and mechanical strength properties of the sintered sample are notably enhanced.

Figure 11. Schematic setup of hot-press sintering (HPS).

Wang et al. enhanced the mechanical strength of mullite matrix composites by adding MWCNTs to $\text{Al}_2\text{O}_3\text{-SiO}_2$. The powders of MWCNTs, Al_2O_3 , and SiO_2 were dispersed and stirred in ethanol, followed with drying and sieving. The sieved powder was hot-pressed at a pressure of 30 MPa and sintered at 1600 °C for 1 h in an Ar atmosphere. The K_{IC} of the HPSeD composites with and without MWCNTs were 2.02 and 3.60 $\text{MPa}\cdot\text{m}^{1/2}$, respectively; the bending strength increased from 466 to 512 MPa [124]. Yuan et al. compared the directional thermal properties of the unidirectional carbon/MWCNTs composite block. They prepared the composite block through mixing MWCNTs with mesophase pitch-based pitch fibers and unidirectional carbon in isopropyl alcohol (IPA), followed by HPS at 500 °C for 5 h with an applied pressure of 4 MPa. They compared the transversal section, the side plane, and the hot-pressed plane for the thermal diffusivity (D). The D values of the block transversal section dropped from 650 to 450 mm^2 with the increase in the MWCNTs, while the side plane and hot-pressed plane showed a value less than 25 mm^2/s and peaked at 3 vol.% MWCNTs [125]. Ding et al. reduced the excessive thermal residual stress of Mg-6Zn through hot-pressing with SiC-catalyzed MWCNT. Ultrasonic vibration and semi-solid mixing were applied to the Mg-6Zn and MWCNTs before the 100 MPa hot-pressing at 700 °C. The thermal residual stress reduced from 74 to 35 MPa and the mechanical strength such as the elastic modulus and elongation were enhanced [126]. Saleem et al. compared the flexural strength of the silicon nitride/silicon carbide composite ($\alpha\text{-Si}_3\text{N}_4/\text{SiC}$) incorporated with 2 wt.% carbon nanostructures (CNS). The incorporated CNSs were CNF, MWCNTs, and graphene nanoplatelets (GNPs). The fabrication of the composite involved ethanol-contained ball milling and 40 MPa hot-pressing at 1700 °C for 1 h. The flexural strength, K_{IC} , and κ_{th} of pristine $\alpha\text{-Si}_3\text{N}_4/\text{SiC}$ were 502 MPa, 7.05 $\text{MPa}/\text{m}^{1/2}$, and 78.44 W/mK, respectively (Figure 12). Meanwhile, a 2 wt.% MWCNTs-added $\alpha\text{-Si}_3\text{N}_4/\text{SiC}$ composite achieved the enhanced properties of 765 MPa, 9.7 $\text{MPa}/\text{m}^{1/2}$, and 99.28 W/mK, respectively [127].

Figure 12. The properties of CNS-reinforced $\text{Si}_3\text{N}_4/\text{SiC}$ CMCs: (a) bulk and relative densities, (b) thermal conductivity, (c) fracture toughness and flexural strength, and (d) Young's modulus and hardness. The composites are labelled as S1 (CNS-free composites), S2 (CNF-CMCs), S3 (MWCNTs-CMCs), and S4 (GNP-CMCs). (Reprinted from ref. [127]).

4.3. Pressureless Sintering (PLS)

Pressureless sintering (PLS) differs from pressure-assisted sintering during the thermal treatment. For pressure-assisted sintering (such as SPS and HPS), the densification process of CNTs-CMCs powder takes place in the furnace during the sintering process. For the PLS route, the CNTs-CMCs mixed powder is uniaxially pressed to pellets before the sintering, with a manual hydraulic press or other pelleting apparatus. Next, the pellet is placed in an electrical/tubular furnace and fired to form the final product. Only during the specific temperature firing/sintering, the high energy breaks the strong covalent and ionic bonding within the ceramics and opens a path for the vacancy diffusion mechanism [128]. The gas type/flow is optional and greatly dependent on the thermal stability and purity of CNTs at different elevating temperatures. The schematic setup is displayed in Figure 13.

Figure 13. Schematic setup of pressureless sintering, a two-step densification. (a) Powder to pellet through uniaxial pressing and (b) gas-filled sintering of pellet.

Ahmad et al. improved the fracture toughness of alumina (Al_2O_3) ceramic by introducing acid-functionalized MWCNTs and magnesia (MgO) powder. Functionalized MWCNTs were dispersed in deionized water containing SDS, which was added with $\gamma\text{-Al}_2\text{O}_3$ and MgO . The dispersion was then dried out, uniaxially compacted at 800 MPa, and sintered at 1600 °C for 1 h. The mechanical properties such as flexural strength and toughness increased by 14.71% and 28.13% but the Young's modulus dropped from 392 to 370 GPa, as compared to pristine Al_2O_3 and $\text{Al}_2\text{O}_3\text{-MgO-MWCNTs}$ [129]. Abden et al. developed excellent-hemocompatibility MWCNTs-hydroxyapatite composites for bone implant application through the PLS technique. The toxicity of MWCNTs is a critical issue when it comes to pharmaceutical application. This composite, which contained 2 wt.% functionalized MWCNTs, was fabricated through 150 MPa cold pressing and 1100–1150 °C vacuum sintering. The composite achieved a H_V of 3.6 GPa through 1100 °C sintering, and the compressive strength and toughness were 481.7 MPa and $2.38 \text{ MPa}\cdot\text{m}^{1/2}$ for the 1150 °C sintered composite. The haemolytic rate of the composite was as low as 1.27%, showing its outstanding hemocompatibility with the human body [130]. Lastly, Muccillo et al. developed a $\text{CeO}_2\text{-Sm}_2\text{O}_3\text{-MWCNTs}$ ceramic with a low impedance through electric-field-assisted PLS. The composite was started with the attrition milling of raw material at 5000 rpm for 1 h (15 min per milling), avoiding the temperature rise and powder agglomeration. Electric-field-assisted PLS heated up the powder-compacted pellet at 850 °C at 1 A of A.C. flow. $\text{CeO}_2\text{-Sm}_2\text{O}_3$ without the addition of MWCNTs recorded the impedance of 3.0 M Ω ; the MWCNTs addition enhanced the ceramic electrical conductivity and the measured impedance was reduced to 16.4 k Ω [131]. Table 7 shows a series of reported CNTs-CMCs fabrication via PLS technique.

Table 7. Previous work on CNTs-CMCs through PLS technique.

Matrix	CNTs Type	Dispersion Procedure	Pelleting and Sintering	Outcome	Reference
Duran® glass powder	MWCNTs	Colloidal	10 MPa Two step: 500 °C (30 min) and 750 °C (3 h)	10 wt.% CNTs-Cristobalite Density: 1.98 g/cm ³ Porosity: 11%	[132]
Al ₂ O ₃	MWCNTs	Chemical mixing and freeze drying	19 MPa 1500 °C, 2 h	1 vol.% CNTs-Al ₂ O ₃ Electrical resistivity: −95.4% Hardness: −3.88% Flexural Strength: +34.74% K _{IC} : +24.24%	[133]
Al ₂ O ₃	MWCNTs	Ball milling Gas purging sonication	375 MPa 1600 °C, 15 min	1 wt.% functionalized CNTs-Al ₂ O ₃ K _{IC} : +9% Young's modulus: +7% Shear modulus: +10.66%	[134]
Al ₂ O ₃	MWCNTs	Wet mixing	50 MPa 1520 °C, 1 h in air	0.1 wt.% MWCNTs-Al ₂ O ₃ ρ%: −1.16% Porosity: +45.93% K _{IC} : −10.18% Grain size reduced 37.23%	[135]
Al ₂ O ₃	MWCNTs SWCNTs	Sonication	50 MPa 1520 °C 1 h	0.1 wt.% SWCNTs-Al ₂ O ₃ ρ%: −3.46% K _{IC} : +13.79% Grain size increased 56.25%	[136]
Silicon coupling agent of KH550	MWCNTs	Silane coupling reaction	2050 °C in Ar	Density 3.1–3.02 g/cm ³ K _{IC} : 3.8–4.1 MPa·m ^{1/2}	[137]

Pressureless sintering is the least complex sintering method where the furnace setup is considerably low cost and simpler as compared to SPS and HPS. However, the inhomogeneous CNT dispersion and the long sintering duration are needed to achieve sufficient time and energy savings.

4.4. Microwave-Assisted Sintering (MAS)

Microwave-assisted sintering emerged as a new sintering technique for CNTs-CMCs fabrication. The processed CNTs-CMCs interact with the electromagnetic field (microwave), where the existence of electric or magnetic fields is highly material-dependent. Microwaves irradiate the CNTs-CMCs and generate heat within the CMC. The generated heat is responsible for the thermophysical changes and the CNTs-CMCs interfacial interactions.

Wang et al. coated SWCNTs with SiC via microwave irradiation at 675 W, on the acidified SWCNTs and the chlorotrimethylsilane (a type of chromatographic agent) [138]. After 10 min of microwave irradiation, the CNTs-silane mixture in the vessel formed a tree-like solid, and the energy dispersive X-ray spectroscopy coupled transmission electron microscope (EDX-TEM) analysis showed that the SiC coated the wall of SWCNTs (see Figure 14a,b). Bhandavat et al. compared the influence of conventional pyrolysis and microwave sintering on the Si(B)CN polymer-derived ceramic with 5 wt.% MWCNTs reinforcement [139]. MWCNTs were first dispersed in toluene and homogenized with boron-modified poly(urea)methyl vinyl silazane (PUVMS, acting as Si(B)CN polymeric precursor) before the thermal treatment. By comparing the microwave sintering (900 W, 5 min) and pyrolysis (800 °C, 4 h), the oxidation temperature of the microwave-sintered CNTs-Si(B)CN ceramic (736.8 °C) was higher than that of the pyrolysis ceramic (730 °C), and the weight loss of the microwave-sintered ceramic was 17.4% lower than that of the pyrolysis ceramic. However, the 5 min microwave sintering provided insufficient time for ceramic growth, resulting in a ceramic yield of only 50%. Abbaspour and Ghaffarinejad

developed CNTs-CCEs for DNA determination by the microwave-assisted sintering of methyltrimethoxysilane (MTMOS) and CNTs at a ratio of 100 μ L:25 mg [140]. They performed low-power microwave irradiation (300 W, 10 min) on the MTMOS-CNTs sol-gel mixture with methanol and HCl as a medium and gelling agent, respectively. This CNTs-reinforced CCE successfully oxidized adenine and guanine in DNA, and the limit of DNA detection was as low as 0.05 μ g/mL. A series of microwave assisted sintered CNTs-CMCs is displayed at Table 8.

Figure 14. (a) Optical image and transmission electron microscopy (TEM) micrograph (inset), and (b) the energy dispersive X-ray spectroscopy (EDX) spectrum of SWCNTs-SiC composite. (Adapted with permission from ref. [138]. Copyright 2006 Elsevier.)

Table 8. Literature database of CNTs-CMCs via microwave-assisted sintering.

Matrix	CNTs Type	Dispersion Procedure	Microwave Parameter	Outcome	Reference
Al ₂ O ₃	MWCNTs	Colloidal processing	900 W, 45 min	Al ₂ O ₃ -1 vol.% CNTs K _{IC} : 3.0–4.1 MPa ^{1/2}	[141]
SiC	SWCNTs	Wet powder processing	900 W, 55 min	SiC-0.5 wt.% CNTs Hardness: +23% κ_{th} : +50% Electrical conductivity: −27%	[142]
Tungsten carbide (WC)	CVD-CNTs	In situ CNTs growth on WO ₃ -Co ₃ O ₄	1200 °C, 10 min	WC and CNTs formed where melamine acted as a C precursor WC attached on the CNTs wall	[143]
Al ₂ O ₃	CVD-CNTs	Wet powder processing	1550 °C	Al ₂ O ₃ -1 wt.% CNTs High heating rate (100 °C/min) Mass loss: +0.35% ρ °: −3.4%	[144]

The heating rate of microwave sintering is not limited as the thermal heating furnace is, which makes this sintering capable of reaching high temperatures rapidly and offers a faster sintering path. Yet, microwave sintering can only be applied to composites with certain criteria: ceramics with low microwave absorbances and low additions of CNTs. This is because high-microwave-absorbance ceramics generate heat rapidly, eventually causing defects in the structure itself; CNT is an excellent microwave absorption material, easily deformed into amorphous/porous carbon or decomposed into gas, leaving a CNT-free ceramic.

5. Enhanced Properties

5.1. Microstructural Properties

The microstructural properties of the pristine CMCs changed upon the addition of CNTs. The introduction of a foreign material (CNT) to the CMCs impacts the grain size, crystallite size, lattice microstrain, unit-cell lattice parameter, and other parameters. Grain size reduction is a common observed phenomenon upon addition of CNTs into CMCs. Through SPS (1800 °C) with colloidal CNT, the grain size growth of Al₂O₃ retards from 75 µm (CNT-free) to approximately 0.2 µm (5 wt.% MWCNTs) [145]. The retardation of grain size is discussed to be due to the CNTs tending to form a strong entangled network surrounding the grain, limiting the grain growth even if a high temperature/energy is supplied for grain growth. Similar research was carried out by Satam et al., where they compared the CNT dispersion process into polycrystalline Al₂O₃: sol–gel versus powder mixing [146]. They recorded 5 vol.% sol–gelled MWCNTs with a higher-homogeneity CNT dispersion showing a greater grain size growth retardation, approximately 69.2% smaller than pristine Al₂O₃, while powder-mixed CNTs only restrained the grain size by about 46.2%. However, both sol–gelled and powder-mixed CNTs–Al₂O₃ enhanced the elastic modulus (E) from 418 GPa (pristine Al₂O₃) to 448 GPa and 434 GPa, respectively. Sharma and Kothiyal reported that the percentage of the crystallite portlandite (trigonal Ca(OH)₂) phase in Portland cement increased from 23.5% to 66.5% with the addition of 0.125 wt.% colloidal MWCNTs cured for 4 weeks [147].

To the best of the authors' knowledge, there is no direct observation of the crystallization mechanism in CNTs–CMCs. However, Wu et al. reported that CNTs induced crystallization in an olefin block copolymer (OBC) by introducing more nucleation sites to the polymer [148]. They observed that the size of crystallite spherulites in the polymer reduced, but the amount of spherulites increased rapidly with the incorporation of MWCNTs. They calculated that the times taken for CNTs-induced spherulites to reach 10% and 50% crystallinities were 33.8 and 37.2 times faster than those for the CNT-free polymer, respectively. The dimensional growth and the nucleation sites of spherulites in polymers can also be estimated with the *n* and *k* values in classic isothermal polymer crystallization kinetics—the Avrami equation [149] in Equation (2):

$$1 - X_t = \exp(-kt^n) \quad (2)$$

where *k* is the crystallization rate constant and *n* is the crystal growth geometry-dependent Avrami exponent. The *k* values of 0.1 wt.% CNTs–OBC and pristine OBC were recorded as 0.0874 and 2.2×10^{-6} , respectively, which indicates that the MWCNTs introduced more nucleation sites and reduced the induction period for OBC crystals. Pristine OBC was categorized as a three-dimensional crystallization growth with an *n* value close to 3 (*n* = 2.84), while CNTs–OBCs were more likely to exhibit two-dimensional crystal growth as the *n* value was 2.41. In addition, the crystallization activation energy of 0.1 wt.% CNTs–OBC was recorded at 422.84 kJ/mol, which is lower than that of pristine OBC, which was recorded at 522.5 kJ/mol. The incorporation of CNTs helped in promoting more nucleation sites, switching the crystal growth to a lower dimension and reducing the activation energy, resulting in a rapid crystallization.

5.2. Thermal Properties

CNTs have a positive influence on the thermal properties of CMCs, namely, thermal conductivity, diffusivity, resistivity, capacity, and the coefficient of thermal expansion. CMCs consist of strong bonds and light atoms e.g., O–Si–O bonds. At *T* > 0 K, the atoms in CMCs vibrate in a collective mode: phonon vibration. Phonon vibrations can be transmitted across or stored in the solid, and these are greatly affected by vibrations of adjacent atoms through bonding and the surrounding temperature, triggering elastic deformation. At working temperatures lower than the Debye temperature (*T* < *T_D*), the Einstein model approximates that the heat transport in a material is the result of high mobility, and the

temperature dependency is T [150]. However, this is nearly negligible for ceramic materials with localized charge. Debye introduced the approximation of heat transport in the form of phonons, and the temperature dependency is T^3 [151], which is applicable in metals, ceramic, glass, etc. [152].

Phonon vibrations are a quantum theory-derived concept that describes the energies and directions of motion in collective modes propagating through the material. The concept of the phonon is analogous to light particles—photons that involve energy and frequency. The photon energy depends on the frequency of the electromagnetic wave (ν), while the phonon energy (ϵ) depends on the velocity of sound (v_s) and wavevector-derived angular frequency (ω).

Phonon–phonon interactions, crystal imperfections, and grain boundaries are the main factors that influence the thermal conduction in CMCs. Thermal energy travels through the ceramic as phonons (elastic waves) at the speed of sound until they are fully scattered. The phonon scattered as a form of wave through phonon–phonon interaction. When the in-phase phonon waves overlap at a particular atom, the vibrational amplitude is superimposed and produces a different phonon with a different spring constant. In addition, phonons scatter at lattice imperfections, especially for materials lacking a periodically arranged lattice. The thermal conductivity (κ_{th}) and diffusivity (D) of CMCs decrease as the crystalline ceramic approaches its melting point. At the melting point, the ordered lattice arrangement in the ceramic starts to distort and form the semi-crystalline and amorphous phase, causing the number of scattering sites to increase. The increased scattering sites give rise to thermal resistivity (ρ) and degrade the κ_{th} and D of the ceramic. By contrast, the dominant mechanisms of the κ_{th} and D are highly dependent on thermal radiation in the form of light at high temperature. At this temperature, ceramic conducts heat through absorbing and emitting photons in a rapid sequence. This thermal conduction mode increases κ_{th} and D values with the increase in working temperature, and this is an important parameter of thermal management in transparent-based glass materials. In addition, the grain size and grain boundaries determine the thermal conduction in ceramics. During the synthesis of ceramics, controllable high temperatures are involved in promoting the grain growth and reducing the grain boundaries. The closer the grains, the faster the phonon vibration or photon transmission between atoms, and this improves the thermal conduction of CMCs.

The thermal capacity (C_p) of ceramics is based on the bond strength, mass of the atom, and bond length. Light atoms in CMCs have a short bond length that contribute as a function of the distance of the potential well, analogous to Hooke's Law. Two spheres are attached to a spring at an equilibrium position, which represents the atom at the bond length (see Figure 15). When the bond is compressed or stretched from its equilibrium position, the short bond length, strong bonding constant, and low mass cause the CMCs to have a high vibration frequency with a small disturbance in the lattice, resulting in a high C_p .

CNTs have introduced their unique thermal transport properties into CMCs by reducing the crystal defects. During the CNTs–CMCs fabrication, CNTs possess a high κ_{th} that channels thermal energy from the heat source into the CMCs crystal, introduce more nucleation sites, reduce the induction period, and enhance the crystallization. The crystals in CMCs appear as single or poly-crystalline instead of amorphous phases. However, CNTs form a network around the ceramic grain, retard the grain growth, and increase the grain boundaries. This may result in a low thermal transport of the CMCs. CNTs fill the grain boundary through tube–tube aggregation and conduct phonon vibration together with electron transmission as CNTs are electron-rich materials. Table 9 shows previous research on applying CNTs to CMCs in achieving better thermal management.

Figure 15. Analogy diagram of high-frequency bond vibrations on how ceramics gain high thermal capacity.

Table 9. Thermal properties of CNTs-CMCs.

Dispersion Process	Densification and Sintering	Outcome *	Reference
Powder	Atmospheric plasma spraying	4 wt.% MWCNTs- Al_2O_3 on Inconel 718 substrate κ_{th} : +117.7% K_{IC} : +13.1%	[153]
Precursor impregnation	Pyrolysis	VACNTs *-CF/SiC κ_{th} : +111.6%	[154]
Powder	High-velocity oxy-fuel coating	8 wt.% CNTs- Cr_2O_3 on T22 steel Corrosion rate: -87.8%	[155]
Powder	Atmospheric plasma spraying	1 wt.% CNTs-YSZ *- $\text{La}_2\text{Zr}_2\text{O}_7$ Thermal cycling: 126 cycles to 218 cycles	[156]
Powder	SPS	4 wt.% CNTs/SiC- Al_2O_3 D: $9 \text{ mm}^2/\text{s}$ κ_{th} : 30.82 W/mK C_p : 0.9 J/gK	[67]
Chemical vapour infiltration	PLS	CNTs-SiC network coated alumina pipe Thermal insulation: $60-12.5 \text{ }^\circ\text{C/min}$ at $750 \text{ }^\circ\text{C}$ flame	[157]

* VACNTs: vertically aligned CNTs; YSZ: yttrium-stabilized zirconia.

5.3. Optical Properties

The optical properties are the behaviour of materials when they are exposed to electromagnetic radiation (light). Glass-based materials are optically transparent, have a high light transmittance, a high reflectance (smooth surface), and a high optical density-dependent refraction. By contrast, glass-ceramics or ceramics-based materials mostly appear as opaque, and the light transmitted through them is nearly zero. When the material interacts with light, the predominant mechanism that occurs in the materials is electronic polarization and electron transition between different energy states.

Electronic polarization takes place during the electric field of light distorting the electron cloud in the material. The electronic polarization mechanism can be divided into two conversions: photon–phonon and photon–photon. In photon–phonon conversion, light energy is scattered and converted into elastic waves during the propagation through the materials. The produced elastic waves appear to be phonon vibration and, subsequently, generate heat. In photon–photon conversion, it involves a rapid light absorption and reemission at the same wavelength, which is known as reflection. As the energy levels of electrons are quantized and the ground state overlaps with the excited state, light provides the electrons with sufficient energy to shift from lower energy levels (ground state) to a higher energy levels (excited state). At the higher energy levels, electrons are unable to hold the energy for prolonged periods and instantly fall back to the ground state, emitting electromagnetic radiation at the same wavelength as the light energy supplied to the electrons. Figure 16 shows the possible phenomenon when ceramics interacts with light.

Figure 16. Light phenomenon when the material is exposed to electromagnetic radiation (light). Transparent samples (glass) refract the incident ray; almost all the material reflects light but at different angles of reflection, i.e., a smooth surface reflects the light at an identical angle; light transmits through translucent and transparent materials (glass–ceramics or ceramics-based materials); high-light-absorption materials absorb light and may scatter as a form of heat (CNTs-added ceramics).

However, electronic polarization is not applicable to most ceramics, as there is a separation (capped at 4 eV) between the valence band and conduction band—the bandgap energy (E_g). Due to the remarkable E_g , the electronic transition in the ceramic is meaningful when it comes to application purposes. E_g is classified into direct and indirect, and the electronic transition is divided into allowed and forbidden transitions. The direct bandgap is a vertical transition (electron–photon interaction) at the same wavevector where the energy changes but the momentum is conserved, e.g., X–X transition; the indirect bandgap is an oblique transition (electron–photon–phonon interaction) at different wavevectors where the energy and the momentum change, e.g., X– Γ transition. The difference between the allowed and forbidden transitions is the momentum matrix element characterization: different from zero (allowed transition) and equals zero (forbidden transition). The sketched band structure of a material with an indirect bandgap is displayed in Figure 17. It shows that the direct E_g is larger than the indirect E_g , meaning that the material is capable of performing a direct band transition when the energy supplied is sufficient. Researchers have extensively applied CNTs to optical absorbance properties such as bandgap reduction to domain crystals. Table 10 shows previous studies in the literature of the application of CNTs in achieving ceramics with low bandgap applications.

Figure 17. Schematic diagram of band structure in a material predominant with indirect bandgaps and other electronic transitions. DF: direct forbidden transition, DA: direct allowed transition, IA: indirect allowed transition, and IF: indirect forbidden transition.

Table 10. The enhanced optical properties in CNTs-CMCs from previous studies in the literature.

Dispersion Process	Outcome *	Reference
Ultrasonication	20 wt.% MWCNTs-TiO ₂ E _g : 2.8–3.1 eV (+10.71%)	[158]
Hydrothermal	5 wt.% MWCNTs-Bi ₂ S ₃ E _g : 1.245–0.875 eV (−29.72%) MB degradation: 60% to 90% Stability after 4 cycles: retain at 75%	[109]
Powder	0.31% CNTs-10% Al ₂ O ₃ -MoTiAl Laser absorptivity: +10.3%	[159]
Colloidal	E _g reduction in CNTs- ferrite 0.1 wt.% CNTs-NiFe ₂ O ₄ : −15.17% 0.1 wt.% CNTs-CoFe ₂ O ₄ : −20.0% 0.1 wt.% CNTs-Ni _{0.4} Co _{0.6} Fe ₂ O ₄ : −11.76%	[160]
Powder	45 wt.% CNTs/CQD-FA-TiO ₂ * E _g : 3.19–3.26 eV (+2.19%)	[161]

* CQD: carbon quantum dot; FA: fluorapatite.

5.4. Mechanical Properties

Introducing CNTs into CMCs to make a stronger ceramic composite is not a modern advancement but it has been developed decades ago. Previous studies in the literature have shown the effect of CNTs on the enhancement of mechanical properties when CNTs are dispersed and densified with appropriate techniques with optimized CNTs compositions. Generally, the CNTs-CMCs mechanical properties enhancement refer to the increase in fracture toughness (K_{IC}), flexural strength, and Young's modulus, upon low CNTs addition. The K_{IC} of the CNTs-CMCs was mainly estimated by measuring the crack lengths from the Vickers indentation (also known as the indentation fracture indentation technique) [120,136,162,163] and single-edge notched beam (SENB) method [51,164–166].

For CNTs-CMCs materials, the Evans and Charles equation [167] is widely used to estimate the K_{IC} from the crack length, which is shown in Equation (3):

$$K_{IC} = 0.0752 \frac{P}{c^{3/2}} \quad (3)$$

where P is the applied load and c is the radial crack length.

The lack of CNT pullout from the CMCs and CNTs bridging caused the Vicker's surface hardness (H_V) and the $q\%$ of the CNTs-CMCs to not show significant improvements, and they increased the risk of mechanical defects such as a low K_{IC} and low bending strength [166] (see Figure 18). Table 11 displays the recent works (dispersion, densification, sintering, and optimized CNTs composition) of the CNTs-CMCs compared with the CNT-free CMCs to illustrate the improvement from the mechanical perspectives.

Figure 18. SEM image and mechanical properties of CNTs-SiC composites. (a) CNTs debonding was observed in the 1 wt.% CNTS-SiC, and (b) CNTs bridging was observed in the 5 wt.% CNTs-SiC. CNTs bridging dissipates the energy under an external load, and it increases the K_{IC} and the bending strength, as shown in (c). (Adapted with permission from ref. [166]. Copyright 2016 Elsevier.)

Table 11. Previous published work on the mechanical improvement of CNTs-CMCs. Compared to the monolithic CMCs, the enhancement % of optimized CNTs-CMCs are calculated unless stated otherwise.

Dispersion	Densification and Sintering	Outcome *	K _{IC} Characterization Technique	K _{IC} Equation	Reference
Wet powder	SPS	0.1 wt.% MWCNTs-Al ₂ O ₃ -MgO-ZrO ₂ H _V : +4.39% from CNTs-free K _{IC} : +3.16%	Vickers indentation	Evans and Charles [167]	[168]
Wet powder	HPS and Exclusion	20 vol.% CNTs-B ₄ C-Al ₂ O ₃ Bending strength: 380 MPa K _{IC} : 4.19 (0.51) MPa·m ^{1/2} H _V : 11.0 (0.21) GPa	Vickers indentation	Miyoshi et al. [169]	[170]
Colloidal	HPS	0.3 wt.% MWCNTs-Al ₂ O ₃ K _{IC} : +8.0%	Vickers indentation	Shetty et al. [171]	[172]
Colloidal	UP-PLS CIP-PLS	0.01 wt.% CNTs-Al ₂ O ₃ -MgO-Y ₂ O ₃ -ZrO ₂ UP-PLSed composites K _{IC} : +41.62% H _V : −9.68% CIP-PLSed Composites K _{IC} : +41.87% H _V : +6.620%	Vickers indentation	Evans and Charles [167]	[173]
Powder	HPS	2.0 wt.% CNTs-SiC-TiB ₂ K _{IC} : −23.73% H _V : +6.93%	Vickers indentation	Evans and Charles [167]	[174]
Powder	HPS	3.85 wt.% CNTs-B ₄ C-ZrC _{0.8} K _{IC} : +68.14% H _V : −35.41%	Vickers indentation	Evans and Charles [167]	[69]
Powder	HPS	2 wt.% MWCNTs-Si ₃ N ₄ -SiC K _{IC} : +37.59% Flexural strength: +52.39% H _V : +16.45%	SENB	n/a	[127]
Colloidal	SPS	7 wt.% MWCNTs-BAS-Si ₃ N ₄ Flexural strength: −22.89% K _{IC} : +31.91%	Vickers indentation	Evans and Charles [167]	[175]

* BAS: barium aluminum silicate; CIP: cold isostatic pressing; UP: uniaxial pressing.

6. Summary and Outlook

The present review article aimed to provide an overview of the critical challenges, the recent breakthroughs on the dispersion and densification and sintering routes, and the enhanced characteristics of the CNTs-reinforced ceramic matrix composites. CNTs have strengthened the ceramic matrix composites in many aspects such as density, fracture toughness, thermal conductivity, and wear resistance, while only a low amount of CNTs reinforcement is needed. Those beneficial properties could be improved or perfected if the CNT fillers are distributed homogeneously within the domain matrices, and the agglomeration issue has thrived. With such fascinating properties, CNTs should have improved the CMCs' functional properties linearly or exponentially with the increase in CNT fillers. However, most research on the CNTs-CMCs has resulted in an "optimum" addition of CNTs for the best CMCs' performance due to the CNTs agglomeration at a large CNTs amount in the matrix.

To counter these issues, researchers have investigated the processing techniques and densification and sintering routes of CNTs-CMCs, such as the sol-gel processing and SPS, to maximize the functional properties. Every mentioned processing technique (Section 3)

and densification and sintering route (Section 4) has its pros and cons in the perspective of the techniques' complexity, duration, energy consumption, and the starting materials (see Tables 12 and 13). All these pros-cons considerations are the parameters that determine the CNTs distribution, interfacial adhesion between CNTs and the domain ceramic, and the thermal stability and the sinterability of CNTs-CMCs. The desired properties of the CNTs-CMCs end-products are also the main concerns during the fabrication process. Still, many studies maintain the momentum to optimize the existing CNTs-CMCs fabrication processes, discover novel fabrication methods, and evaluate the final composites' performance from the microstructural properties to the functional properties before commercializing them. We addressed the fundamental insights for the future technological maturation and advancement of CNTs-CMCs.

Table 12. Comparison table of processing methods.

Processing Technique	Powder	Colloidal	Sol-Gel	In-Situ CNTs Growth	Hydrothermal
Duration	Within hours	Within hours	Several hours—several days	Several hours	Several hours—several days
Temperature (°C)	Ambient	Ambient	Ambient—200	>600	100–250
Advantage	No or minimum chemical involved	Rapid processing	Forming CNTs network	High interfacial adhesion	Homogenous domain crystal growth
Disadvantage	Inhomogeneous CNTs dispersion	CNTs structural defect	Long processing duration	Inconsistent CNTs yield	Long processing duration

Table 13. Comparison table of the densification and sintering techniques.

Densification and Sintering	Spark Plasma Sintering (SPS)	Hot-Press Sintering (HPS)	Pressureless Sintering (PLS)	Microwave-Assisted Sintering (MAS)
Duration	Within minutes	Minutes to hours	Several hours	Within 30 min
Advantage	Rapid sintering	Short sintering duration	Low setup cost	Rapid sintering
Disadvantage	High-energy consumption	High-energy consumption	Inhomogeneous CNTs dispersion	Low CNTs addition only

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Abbreviations

CCE	Carbon ceramic electrode
CMCs	Ceramic matrix composites
CNTs	Carbon nanotubes
CNTs-CMCs	Carbon nanotube-incorporated ceramic matrix composites
CVD	Chemical vapour deposition
D	Thermal diffusivity
EG	Ethylene glycol
E _g	Optical band gap energy
HNO ₃	Nitric acid
HPS	Hot-press sintering
H _v	Vicker's surface hardness
K _{IC}	Fracture toughness
MAS	Microwave-assisted sintering
MWCNT	Multi-walled carbon nanotube
PLS	Pressureless sintering
PVP	Polyvinyl pyrrolidone
SPS	Spark plasma sintering
SWCNT	Single-walled carbon nanotube
κ _{th}	Thermal conductivity
ρ%	Relative density

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