Alumina–MWCNT composites: microstructural characterization and mechanical properties

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ABSTRACT

In the present work, Al₂O₃–multiwalled carbon nanotube (MWCNT) composites have been developed by both conventional sintering and spark plasma sintering (SPS) and their microstructures, mechanical properties and wear behavior have been investigated. Further, the influence of various other parameters such as the sintering time, sintering temperature, MWCNT loading level and processing technique adopted for development of the composites has also been analyzed. The powder metallurgy route was selected for development of Al₂O₃–0.2, 0.5, 0.8, 3, 5 vol% MWCNT composites using both conventional sintering and SPS. For conventionally sintered Al₂O₃–MWCNT composites, it has been found that both the hardness and relative density of the composites decreased up to a loading level of 0.2 vol% of MWCNTs, followed by a continuous increase with the addition of MWCNTs to the Al₂O₃ matrix, attaining a maximum value in the case of Al₂O₃–3 vol% MWCNT composite. The wear behavior of conventionally sintered composites also exhibits significant improvement with increase in sintering time. The SPSed Al₂O₃–MWCNT composites show a much higher relative density and better mechanical and tribological properties as compared to conventionally sintered Al₂O₃–MWCNT composites.

1. Introduction

The substantial progress in ceramic-based nanocomposites (CMNCs) is playing a vital role in broadening the range of areas in which ceramics can be applied. Alumina (Al₂O₃)-based composites are potential engineering materials possessing superior mechanical as well as tribological properties. Monolithic ceramics suffer from inherent brittleness, poor creep resistance and low fracture toughness. Considerable number of attempts have been made over the last few decades to develop ceramic-matrix composites (CMCs) with better mechanical properties as compared to monolithic ceramics [1,2]. CMCs have low weight, high hardness, and superior thermal and chemical resistance, and they have emerged in recent years, as an attractive choice for a wide range of applications. Since Niihara introduced the concept of nanocomposites in 1991 [3], the addition of nanofillers as a reinforcement phase has become one of the most promising methods of improving the mechanical properties of CMNCs. Carbon nanotubes (CNTs) have emerged as potentially attractive nanofillers for CMNCs. In the present work, multiwalled carbon nanotubes (MWCNTs) have been used as reinforcement for the development of Al₂O₃–MWCNT composites. The density of MWCNTs is ~2.6 gm/cc, and their specific surface area lies in the range of 200–400 m²/g. The tensile strength of MWCNTs ranges between 10 and 60 GPa whereas its modulus lies in the range of 0.3–1 TPa. It has high thermal conductivity of ~3000 W/m K and exceptional electrical conductivity in the range of 10⁶–10⁷ S/m [4]. Al₂O₃ is one of the most commonly used ceramic materials due to its extremely high hardness (15–22 GPa), high oxidation resistance and good chemical stability. Among the various engineering ceramics, Al₂O₃ is one of the most cost-effective and economically viable materials. Al₂O₃ possesses an extremely high melting point of ~2071°C and its density lies in the range of 3.75–3.95 gm/cc. Apart from these attributes, its bulk modulus is ~324 GPa, its Young’s modulus is ~413 GPa and its compressive strength lies in the range of 2000–4000 MPa. The fracture toughness of Al₂O₃ is ~5 MPa√m and its coefficient of thermal expansion is 10.9 × 10⁻⁶/K [5]. Although Al₂O₃ has several excellent functional properties, its applications are limited due to its low fracture toughness. Significant efforts have been made to improve the fracture toughness of Al₂O₃ by the addition of nanofillers or the use of new sintering processes such as spark plasma sintering (SPS) [6,7]. Despite the tremendous efforts exerted in the area of composites, however, uniform dispersion of the nanofillers in the ceramic matrix is still a key challenge. The difficulties associated with the homogeneous distribution of nanofillers and reproducible development of materials possessing enhanced mechanical properties could be considered the major hindrance in the area of
nanocomposites [8,9]. Renewed interest in CMCs was observed with the discovery and commercial availability of carbonaceous nanofillers such as CNTs and graphene [10,11]. The outstanding functional characteristics and exceptional mechanical properties of CNTs make them an attractive choice as nano-reinforcements to improve the fracture toughness of brittle ceramics.

To date, extensive research has been conducted to enhance the fracture toughness of ceramic-based materials. Many atomistic simulations have predicted that CNTs possess a capability of enduring significant tensile and compressive forces prior to failure due to their unique morphology and considerable flexibility. The addition of CNTs as nanofillers can not only enhance the hardness and strength of the composites but can also enhance their wear resistance. Due to their closed tubular structures, CNTs form a weak interaction at the matrix interface during the wear process [12]. However, CNT-reinforced CMNCs developed to date have exhibited much lower mechanical performance than expected. This might primarily be attributable to the agglomeration of CNTs and weak interfacial bonding between the nanotubes and the matrix. The effectiveness of CNTs in reducing the wear rate and providing a stable coefficient of friction has been validated experimentally under different loading conditions for carbon-reinforced composites [13,14]. A study on Al2O3–CNT composites describing the effects of CNTs on their mechanical characteristics and electrical performance has been conducted earlier [15,16] and the effects of CNT addition on the tribological properties have also been reported [17]. Significant enhancement of wear resistance with the addition of CNTs has been observed. However, a detailed understanding of the tribological behavior of Al2O3–CNT composites will require further research. This paper reports the influence of MWCNT addition on such properties as the density, hardness, fracture toughness and wear behavior of both conventionally sintered and SPSed Al2O3–MWCNT composites.

2. Materials and methods

2.1. Synthesis of MWCNTs

For the fabrication of various Al2O3–MWCNT composites, a low-pressure chemical vapor deposition (LPCVD) technique was used to synthesize MWCNTs. Due to high van der Waals interactions and a high aspect ratio, achieving uniform dispersion of MWCNTs in ceramic matrices presents major difficulties that can lead to MWCNT agglomeration. To combat this issue, surface modification of MWCNTs has been achieved through acid functionalization. Synthesized MWCNTs were treated with strong oxidizing agents such as H2SO4 and HNO3 in order to reduce the high van der Waals forces and minimize the MWCNT agglomeration and thus to enhance their dispersion in the Al2O3 matrix. Figure 1 shows a schematic diagram of the LPCVD technique used to synthesize MWCNTs along with the acid functionalization procedure.

2.2. Fabrication of Al2O3–MWCNT composites

The powder processing route was adopted to fabricate Al2O3–MWCNT composites. It is well known that MWCNTs tend to agglomerate in the host matrix due to their structural morphology, which leads to an ill-constructed interface between the matrix and MWCNTs. Thus, homogenous dispersion

Figure 1. (a) LPCVD setup used for the synthesis of MWCNTs, (b) route followed for the synthesis of MWCNTs and (c) functionalization of MWCNTs.
of MWCNTs within the ceramic matrix is extremely important in order to impart the desired mechanical properties to composites. The detailed procedures followed for fabrication of Al$_2$O$_3$–MWCNT composites from their milled-powder mixtures are illustrated in Figure 2.

2.3. Consolidation and sintering

For the consolidation of Al$_2$O$_3$–MWCNT composites, both pressure-free and pressure-assisted sintering routes were selected. Pure Al$_2$O$_3$ and Al$_2$O$_3$–0.2, 0.5, 0.8, 3 and 5 vol% MWCNT composites were fabricated. In the case of conventional sintering, green compacts were prepared in a uniaxial cold compaction machine under a load of ~395 MPa and later sintered at 1650°C for three different holding times of 1, 2 and 3 h in an inert Ar atmosphere. For the pressure-assisted sintering, SPS was carried out using a Dr. Sinter 515S apparatus (SPS Syntex Inc., Kanagawa, Japan) with a pulse on–off ratio of 12:2. The various sintering parameters adopted during the SPS of Al$_2$O$_3$–MWCNT composites were as follows:

Temperature = 1450°C, time = 10 min, heating rate = 100°C/min, pressure = 50 MPa, diameter of graphite die = 15 mm, vacuum in chamber = 6 Pa, ambience = Ar (at flow rate of 2 L/min), voltage = 20 V and current flow = ~1200 A.

After sintering, the pressure was removed and the samples were allowed to cool naturally in the furnace until they attained room temperature. Figure 3 shows the SPS profile used for the fabrication of various Al$_2$O$_3$–MWCNT composites.

The Archimedes' method was used to determine the bulk density of various composites, and the rule of mixtures was followed to calculate their theoretical density. The density of Al$_2$O$_3$ was assumed to be 3.95 g/cc and the density of MWCNT to be 2.6 g/
The morphology of the fabricated composites was analyzed under an optical microscope and SEM.

**2.4. Characterization techniques**

Several techniques were used to characterize the synthesized MWCNTs, milled Al$_2$O$_3$–MWCNT powder mixtures and sintered Al$_2$O$_3$–MWCNT composites. The x-ray diffraction (XRD) of the MWCNTs, milled powder mixtures and fabricated composites was conducted using a Panalytical PW 3040 X’Pert MPD X-ray diffractometer using CuKα radiation (λ = 0.15415 nm). A JEOL JEM-2100 high-resolution transmission electron microscope (HRTEM) at an acceleration voltage of 200 keV was used to analyze the morphologies of the blended powder mixtures. The morphologies of the sintered composites were analyzed using a Zeiss Axio Scope.AI optical microscope, a Nova NanoSEM 450/FEI field emission scanning electron microscope (FESEM) and a JEOL-JSM-6480LV scanning electron microscope (SEM), both of the units enabled with energy-dispersive X-ray (EDX) analysis systems. In order to determine the thermal stability of various powder mixtures, differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) were conducted using a Netsch STA 409C Simultaneous Thermal Analyzer at a heating rate of 10° C/min in an Ar atmosphere. A Malvern Nano Zetasizer ZS system was used for the particle size analysis.

**2.5. Mechanical testing**

The mechanical properties of pure sintered Al$_2$O$_3$ and various Al$_2$O$_3$–MWCNT composites were investigated.

For pure Al$_2$O$_3$ and various Al$_2$O$_3$–based composites, the hardness values were measured on a polished cross-section using a Vickers microhardness tester for 10 s. Loads of 100 and 500 gf were applied to conventionally sintered and SPSed composites, respectively. An average of five indentions was considered for each sample. The sizes of the conventionally sintered and SPSed samples were 5 mm × 10 mm and 5 mm × 15 mm, respectively. The single-edge notched beam method under ambient conditions was adopted to determine the fracture toughness of the composites. Due to sample size restrictions, the indentation fracture toughness testing technique was adopted and carried out at different loads to create a notched crack at the indented point. A notched crack with the length l and diameter 2a was formed by the application of stresses in the range of 500–2000 kgf, with the force applied till a complete fracture of the sample was achieved. A crosshead speed of 0.05 mm/min and a maximum span length of 10 mm were set for the toughness test. For a particular indentation load (P), corresponding hardness (H) values were recorded from the point of notch initiation until the complete fracture of the sample. The $K_{IC}$ values were determined by the Shetty equation using the Palmqvist crack model [18,19]:

$$K_{IC} = 0.0899 \left( \frac{H 	imes P}{4l} \right)^{0.5}$$

In order to investigate the wear mechanism and determine the wear performance of pure Al$_2$O$_3$ and various Al$_2$O$_3$–based composites, the dry sliding wear test was carried out using a DUCOM TR208-M1 ball-on-plate tribometer at a sliding speed of 20 rpm and sliding time of 10 min. The wear test was done under a normal load of 1 kgf using a diamond indenter with a diameter of 2 mm and wear tracks 6 mm in diameter were formed on the surfaces of various samples. The variations in the wear rate and wear depth with respect to the sliding time were investigated. SEM was used to characterize the morphologies of the worn surfaces and the wear debris obtained from the wear tracks.

**3. Results and discussion**

Figure 4(a,b) show SEM images of pure alumina (Al$_2$O$_3$) powder used for the fabrication of various Al$_2$O$_3$–MWCNT composites. From the SEM images, it is evident that Al$_2$O$_3$ particles have rough surfaces and that they are equiaxed, with diameters in the range of ~80–140 µm. The porous morphology of Al$_2$O$_3$ particles is shown in the inset image accompanying Figure 4(b). The EDX analysis of the Al$_2$O$_3$ particles in Figure 4(a) suggests that the composition of pure Al$_2$O$_3$ particles is 24.48% Al and 75.52% O. Figure 4(c,d) are SEM images of the MWCNTs used as nanofillers for the fabrication of various Al$_2$O$_3$–MWCNT composites. The hollow cylindrical morphology of the MWCNTs is revealed in the HRTEM image in Figure 4(e). The MWCNTs are found to be composed of concentric cylindrical graphene layers with interlayer spacing of 0.34 nm. The outer diameter of the MWCNTs is ~12 nm and the inner diameter is ~3.3 nm whereas the thickness of the MWCNT walls is observed to be ~4.03 nm. Figure 4(f–h) are SEM images of Al$_2$O$_3$–0.5, 0.8, 5 vol% MWCNT powder mixtures. The SEM images in Figure 4(f,g) show uniform mixing of the Al$_2$O$_3$ particles and MWCNTs. Addition of a low vol% of MWCNTs leads to uniform mixing of Al$_2$O$_3$ and MWCNTs. On the other hand, the SEM image of Al$_2$O$_3$–5 vol% MWCNT powder mixture in Figure 4(h) shows large agglomerates of MWCNTs entangled and clustered with Al$_2$O$_3$ particles. A higher concentration of MWCNTs prompts their agglomeration, which results in nonuniform densification of the composites and deterioration of their mechanical properties [20].

Figure 5 shows HRTEM images of various Al$_2$O$_3$–MWCNT powder mixtures. As the loading level of
MWCNTs was very low in the case of the Al\textsubscript{2}O\textsubscript{3}–0.2 vol % MWCNT powder mixture, no prominent MWCNTs were visible in Figure 5(a). However, in Figure 5(b–e), both MWCNTs and Al\textsubscript{2}O\textsubscript{3} nanoparticles can be clearly observed in the milled powder mixtures. MWCNTs with hollow cores can be easily seen adhering to Al\textsubscript{2}O\textsubscript{3} particles. Both the Al\textsubscript{2}O\textsubscript{3} and MWCNTs were blended by ball milling in the desired volume fractions for a period of 30 min in order to obtain uniformly dispersed powder mixtures. The HRTEM images reveal that the graphitic structure of MWCNTs was well preserved during blending and that the short milling duration did not cause deterioration of the structure of MWCNTs. The presence of nanostructured Al\textsubscript{2}O\textsubscript{3} particles in the blended powder mixture is confirmed by the images. Due to its high brittleness, micron-sized Al\textsubscript{2}O\textsubscript{3} was reduced to the nanometric domain within a short duration of milling.

The hexagonal spot pattern in Figure 6(a) corresponds to the MWCNTs in the Al\textsubscript{2}O\textsubscript{3}–3 vol % MWCNT powder mixture. The SAD pattern of MWCNTs confirms the sixfold symmetry of the carbon atoms positioned in the graphitic lattice. On the other hand, the faint concentric rings seen in the SAD
pattern of the Al₂O₃–5 vol% MWCNT powder mixture in Figure 6(b) correspond to the nanostructured Al₂O₃ in the powder mixture [21,22].

Figure 7(a) shows a DF HRTEM image of Al₂O₃–3 vol% MWCNT powder mixture. It is evident from the combined elemental maps of Al, O and C in Figure 7(b) that both Al₂O₃ particles and MWCNTs were homogeneously mixed. Well-preserved MWCNTs were found sticking to the Al₂O₃ particles. The elemental map of C in Figure 7(c) clearly shows that the MWCNT bundles were enclosed within the Al₂O₃ particles. However, few MWCNTs were observed to remain isolated with no agglomeration. The elemental maps of Al in Figure 7(c) and O in Figure 7(d) correspond to the Al and O atoms of the Al₂O₃ matrix [23].

**Figure 6.** SAD patterns of (a) Al₂O₃–3 vol% MWCNT and (b) Al₂O₃–5 vol% MWCNT powder mixture.

**Figure 7.** (a) DF HRTEM image of Al₂O₃–3 vol% MWCNT powder mixture. Elemental map of (b) Al + O + C, (c) Al, (d) O and (e) C in the HRTEM image (a).

**Figure 8.** (a) DSC and (b) TGA of Al₂O₃–MWCNT powder mixtures.
The thermal stability of Al$_2$O$_3$–MWCNT powder mixtures was analyzed by DSC/TGA. The endothermic peak at ~92°C in the DSC plots of Al$_2$O$_3$–MWCNT powder mixtures in Figure 8(a) corresponds to the removal of the hydroxyl groups and the evaporation of the absorbed moisture. An exothermic peak corresponding to the combustion of MWCNTs can be seen at ~761°C. By comparing the DSC plots of different Al$_2$O$_3$–MWCNT powder mixtures with different MWCNT loading levels, it is observed that the exothermic peak at ~761°C is strongest for the Al$_2$O$_3$–5 vol% MWCNT powder mixture due to its highest content of MWCNTs, resulting in the release of a larger amount of energy because of the higher degree of MWCNT oxidation. The DF HRTEM images in Figure 7 reveal that MWCNTs were well preserved in the form of tiny bundles between the Al$_2$O$_3$ particles at a loading level of 3 vol%, which suggests that complete decomposition of the MWCNTs entrapped between the Al$_2$O$_3$ particles was not achieved in the case of the Al$_2$O$_3$–3 vol% MWCNT powder mixture. Thus, no prominent exothermic peak is visible in the DSC plot of the Al$_2$O$_3$–3 vol% MWCNT powder mixture. It can be noted from the TGA plots of various Al$_2$O$_3$–MWCNT powder mixtures in Figure 8(b) that the mass loss of the powder mixtures occurs in steps. Initially, at ~137°C, the toluene used as a process controlling agent during milling and the residual moisture of the Al$_2$O$_3$–MWCNT powder mixture evaporate. Thereafter, a mass loss corresponding to the combustion of MWCNTs takes place at ~625°C. In the case of the Al$_2$O$_3$–5 vol% MWCNT powder mixture, a large amount of MWCNTs remain entrapped between the Al$_2$O$_3$ particles. As a result, a comparatively smaller mass loss is observed for the Al$_2$O$_3$–5 vol% MWCNT powder mixture than for the powder mixtures with lower MWCNT content. It should be noted that the Al$_2$O$_3$–5 vol% MWCNT composite powder shows more residual mass as compared to the Al$_2$O$_3$–0.5 vol% MWCNT powder mixture because complete decomposition of the entrapped MWCNTs could not be achieved. The TGA plots suggest that the removal of residual moisture and toluene (at ~137°C) shows a relatively more dominant effect on the mass loss of various powder mixtures as compared to the decomposition of MWCNTs. Although the highest mass loss is observed for the Al$_2$O$_3$–0.5 vol% MWCNT powder mixture and the lowest mass loss is observed for the Al$_2$O$_3$–5 vol% MWCNT powder mixture, it is noteworthy that the patterns of both the DSC and TGA plots are alike for all the powder mixtures, indicating that the thermal behavior of all the Al$_2$O$_3$–MWCNT powder mixtures is identical [24,25].

One of the most important physical properties of particulate samples is particle size distribution (PSD). The PSDs of pure Al$_2$O$_3$ and Al$_2$O$_3$–MWCNT powder mixtures were determined by dynamic laser scattering, and the dispersion condition was evaluated based on the zeta potential. The PSD of Al$_2$O$_3$–MWCNT powder mixtures was determined in order to find out the average particle size of the various powder mixtures. The PSD of pure Al$_2$O$_3$ milled for 30 min in Figure 9(a) shows that the average size of the Al$_2$O$_3$ particles is ~2.131 µm. It should be noted that the as-received pure Al$_2$O$_3$ has a particle size in the range of ~80–140 µm (refer to Figure 4(a)). This confirms that a short period of milling can reduce the particle size of Al$_2$O$_3$ to a very fine size. By comparing all the PSD plots in Figure 9(b–f), it is evident that the average particle size of the Al$_2$O$_3$–MWCNT powder mixture becomes lower with increase in the volume fraction of MWCNTs in Al$_2$O$_3$. The reduction in the particle size of the powder mixture corresponds to the increase in the volume fraction of MWCNTs with a very fine size. It should be noted that only a single sharp peak is seen in the PSDs of most of the powder mixtures, whereas two adjacent peaks are seen only in the case of the Al$_2$O$_3$–0.8 vol% MWCNT powder mixture. This confirms the highly uniform PSD in all the powder mixtures [26].

The XRD plots of pure Al$_2$O$_3$ and MWCNTs are shown in Figure 10(a). Sharp peaks located at 2θ values of 28.27°, 38.31° and 49.06° can be seen in the XRD plot of Al$_2$O$_3$. The XRD spectrum of MWCNT shows the strongest peak at 2θ ~26.2° corresponding to the (0 0 2) plane and a low intensity peak at 2θ ~43.9° corresponding to the (1 0 0) plane of MWCNTs. Figure 10(b) shows the XRD patterns of various Al$_2$O$_3$–MWCNT powder mixtures obtained by blending Al$_2$O$_3$ and MWCNTs in a planetary ball mill for 30 min. A reduction in the intensity of the Al$_2$O$_3$ peaks was observed due to the decrease in the crystallite size of Al$_2$O$_3$ during ball milling. As a result, some of the peaks of Al$_2$O$_3$ seen in the XRD plot of the as-received Al$_2$O$_3$ powder are not seen in the XRD plot of the milled Al$_2$O$_3$ and milled Al$_2$O$_3$–MWCNT powder mixtures. Al$_2$O$_3$ is highly brittle in nature and can be reduced to very fine particles by milling for a very short period of time. The (0 0 2) peak of MWCNTs can be clearly seen in the XRD spectrum of all the Al$_2$O$_3$–MWCNT powder mixtures with higher loading levels of MWCNTs [27].

The emergence of new phases and grain growth occurring in the developed composites has been analyzed by XRD. The formation of new peaks in the XRD spectra enables new phase formation or transformation occurring during sintering of the composites to be determined. Figure 11(a) shows the XRD patterns of conventionally sintered pure Al$_2$O$_3$ as well as various Al$_2$O$_3$–MWCNT composites developed at 1650°C for a period of 3 h. Many new peaks emerged
after sintering of the Al$_2$O$_3$–MWCNT composites which were not present in the XRD plots of the Al$_2$O$_3$–MWCNT powder mixtures in Figure 10(b). Sharper peaks of Al$_2$O$_3$ were also observed in the XRD plots of the sintered composites due to grain growth during sintering. Both pure Al$_2$O$_3$ and Al$_2$O$_3$–MWCNT powder mixtures were milled for a period of 30 min, reducing the Al$_2$O$_3$ particles to fine grains, due to which the low-intensity peaks of Al$_2$O$_3$ disappeared. During subsequent sintering of the powder mixtures, coarsening of the Al$_2$O$_3$ grains takes place, resulting in the reemergence of the low-intensity peaks which had disappeared earlier during milling.

Figure 11(b) shows the XRD plots of SPSed Al$_2$O$_3$–MWCNT composites. The XRD peaks of Al$_2$O$_3$ in the SPSed samples show a much lower intensity as compared to the conventionally sintered samples, indicating much lower grain growth. This is due to the much shorter sintering time during SPS as compared to the longer duration of conventional sintering. The (0 0 2) peak corresponding to MWCNTs shows a higher intensity suggesting a greater degree of crystallinity for MWCNTs in the SPSed composites. In the case of SPSed Al$_2$O$_3$–0.8, 3 vol% MWCNT composites, however, a relatively lower intensity of Al$_2$O$_3$ peaks can be seen. This occurs due to the effective grain pinning by MWCNTs at these loading levels. The addition of 0.8, 3 vol% MWCNTs leads to uniform distribution of the nanofiller in the Al$_2$O$_3$ matrix and effectively suppresses the grain growth.
The addition of a higher loading level of MWCNTs leads to its agglomeration in the Al₂O₃ matrix, however, resulting in abnormal Al₂O₃ grain growth. The MWCNTs at the grain boundaries wrap around the Al₂O₃ grains, pin them and act as diffusion barriers. The grain pinning effect can be clearly seen in the SPSed samples but is not prominent for conventionally sintered samples. Also, no profound peak shift was observed for the SPSed samples as compared to the conventionally sintered samples. The shift in the Al₂O₃ peaks seen in the inset images in Figure 11(a,b) corresponds to the diffusion of small C atoms into the Al₂O₃ lattice. The short sintering duration in the case of SPSed samples restricts diffusion, whereas the longer holding time during conventional sintering enables easy diffusion of C atoms [28].

Figure 12 shows optical micrographs of pure Al₂O₃ and the various Al₂O₃–MWCNT composites developed by conventional sintering and SPS. A dense smooth surface is evident in the optical micrographs of pure Al₂O₃ in Figure 12(a–d), conventionally sintered at 1650°C with a holding time of 1, 2 and 3 h, and SPSed at 1450°C for 10 min. For the conventionally sintered pure Al₂O₃ samples, a relative density in the range of ~86.9–89.44% was achieved, whereas a relative density of ~99.24% was observed for the SPSed pure Al₂O₃ sample (refer to Figure 15).

From the optical micrographs of Al₂O₃–MWCNT composites in Figure 12(e–t), it is evident that with the addition of MWCNTs to the Al₂O₃–MWCNT composites, the MWCNTs start to agglomerate. The size of the MWCNT agglomerates was found to increase with increase in the MWCNT content. Large agglomerates with sizes in the range of ~1100–1700 µm can be observed in the optical micrograph of the Al₂O₃–5 vol% MWCNT composite in Figure 12(q–s), whereas in Figure 12(e–g), agglomerates of MWCNTs with a much smaller size in the range of ~73–331 µm are observed for the Al₂O₃–0.5 vol% xGnP composite. It should also be noted that an increase in the dwell time during conventional sintering increases the sizes of MWCNT agglomerates in the composites. In the case of the SPSed samples, MWCNTs were found homogeneously dispersed in the Al₂O₃ matrix due to the short sintering period during SPS, which resulted in uniform grain growth and even distribution of MWCNTs in the sintered composites. The SEM images of SPSed Al₂O₃–0.5 and 0.8 vol% MWCNT composites confirm the uniform distribution of MWCNTs in the Al₂O₃ matrix. On the other hand, conventionally sintered Al₂O₃–0.5 and 0.8 vol% MWCNT composites show few agglomerates of MWCNTs in the Al₂O₃ matrix, a result attributed to abnormal grain growth of Al₂O₃ during conventional sintering leading to the formation of MWCNT agglomerates at the grain boundaries. Upon increasing the MWCNT loading level, however, the size of the MWCNT agglomerate increases irrespective of the sintering technique, as can be seen in the optical micrographs in Figure 12(q–t) [29].

Figure 13 shows FESEM images of pure sintered Al₂O₃ and Al₂O₃–3 and 5 vol% MWCNT composites developed by conventional sintering at 1650°C for...
| Sample                  | 1650°C, 1 h | 1650°C, 2 h | 1650°C, 3 h | 1450°C, SPS |
|------------------------|-------------|-------------|-------------|-------------|
| Pure Al₂O₃             | (a)         | (b)         | (c)         | (d)         |
| Al₂O₃-0.5 vol. % MWCNT | (e)         | (f)         | (g)         | (h)         |
| Al₂O₃-0.8 vol. % MWCNT | (i)         | (j)         | (k)         | (l)         |
| Al₂O₃-3 vol. % MWCNT   | (m)         | (n)         | (o)         | (p)         |
| Al₂O₃-5 vol. % MWCNT   | (q)         | (r)         | (s)         | (t)         |

Figure 12. Optical images of conventionally sintered and SPSed (a–d) pure Al₂O₃, (e–h) Al₂O₃-0.5 vol% MWCNT, (i–l) Al₂O₃-0.8 vol% MWCNT, (m–p) Al₂O₃-3 vol% MWCNT and (q–t) Al₂O₃-5 vol% MWCNT composites.

| Sample                  | Pure Al₂O₃ | Al₂O₃-3 vol. % MWCNT | Al₂O₃-5 vol. % MWCNT |
|------------------------|------------|----------------------|----------------------|
| 1650°C, 1 h            | (a)        | (d)                  | (g)                  |
| 1650°C, 3 h            | (b)        | (e)                  | (h)                  |
| 1450°C, SPS            | (c)        | (f)                  | (i)                  |

Figure 13. FESEM images of (a–c) pure Al₂O₃, (d–f) Al₂O₃-3 vol% MWCNT and (g–i) Al₂O₃-5 vol% MWCNT composites developed by conventional sintering and SPS.
durations of 1 and 3 h and SPSed at 1450°C for a dwell time of 10 min. From the micrographs in Figure 13(a,b), the effect of sintering parameters such as dwell time, temperature and processing technique, along with the influence of MWCNT addition on the grain size of Al₂O₃, can be analyzed. A significant grain growth in conventionally sintered pure Al₂O₃ is clearly visible. SPS restricted the grain growth of Al₂O₃ due to the short sintering duration, however, as can be seen in Figure 13(c). Upon addition of MWCNTs, a remarkable reduction in the Al₂O₃ grain size can be observed from the micrographs. In Figure 13(d), a homogeneous distribution of MWCNTs at the optimum loading level of 3 vol% effectively restricted the grain growth of Al₂O₃ by pinning the grain boundaries. MWCNTs present at the grain boundaries reduced the atomic diffusion coefficient and prevented the grain growth of the host matrix. From Figure 13(e), it is evident that increasing the holding time during conventional sintering embeds MWCNTs within the Al₂O₃ matrix and forms bridges to link the nearby grains, which limits grain growth. The well-sintered Al₂O₃–MWCNT conglomerates in Figure 13(f) correspond to the relatively high densification of Al₂O₃–3 vol% MWCNT composite as compared to the densification of Al₂O₃–5 vol% MWCNT composite prepared under similar sintering conditions (Figure 13(i)). This can be attributed to agglomeration of MWCNTs in the Al₂O₃ matrix at the higher loading level of 5 vol%, which leads to abnormal Al₂O₃ grain growth and reduces the densification of the sintered composite. Abnormal Al₂O₃ grain growth is clearly visible in the micrograph of conventionally sintered Al₂O₃–5 vol% MWCNT composite in Figure 13(g,h).

Figure 14(a) shows an SEM image of a conventionally sintered Al₂O₃–3 vol% MWCNT composite developed at 1650°C with a holding time of 3 h, along with elemental maps of Al, O and C. A white colored lump of Al₄C₃ can be seen lying on the surface of the composite. In the SPSed Al₂O₃–3 vol% MWCNT composite, rod-like Al₄C₃ structures can be seen on its surface. Al₄C₃ is formed by a reaction of MWCNTs with Al₂O₃. The diameter of these rods is ~270 nm. The high pressure applied during SPS along with the short sintering time allowed the formation of these rod-like structures. On the other hand, in the case of conventionally sintered Al₂O₃–3 vol% MWCNT composites, the Al₄C₃ structures are irregular in shape and are not nanostructured due to the prolonged sintering time [30].

As ceramics require very high sintering temperatures, achieving near full density of the composites without damaging the structure and morphology of the MWCNTs is one of the most important challenges during the development of CMNCs. The highest level of densification in Al₂O₃–MWCNT composites can be achieved at an optimum loading level of the nanofiller, as a very high loading level of MWCNTs would lead to their agglomeration in the Al₂O₃ matrix resulting in poor densification of the CMNCs. Agglomerates of MWCNTs at the grain boundaries lead to abnormal grain growth and poor densification of the composites. On the other hand, a very low nanofiller loading level can leave many of the pores unfilled and result in a lower relative density of the composites. Therefore, an optimum nanofiller loading level results in the highest level of densification in CMNCs [31]. Figure 15 shows variations in relative density with respect to the vol% of MWCNTs for various Al₂O₃–MWCNT composites developed under different sintering conditions.

The relative density of conventionally sintered pure Al₂O₃ was found to be in the range of ~86.90–89.44%, whereas pure Al₂O₃ sample developed by SPS had a density of ~99.24%. For the conventionally sintered samples, the density of the Al₂O₃
MWCNT composites was found to improve when MWCNTs were introduced into the Al$_2$O$_3$ matrix in the range of 0.5–3 vol%. However, increasing the loading level of the MWCNTs beyond 3 vol% led to a decrease in the relative density of the Al$_2$O$_3$–MWCNT composites. The highest relative density was obtained for Al$_2$O$_3$–3 vol% MWCNT composites developed under both sintering conditions. The relative density of conventionally sintered Al$_2$O$_3$–3 vol% MWCNT composite fabricated at 1650°C for 3 h was ~94.45%, whereas the density of SPSed Al$_2$O$_3$–3 vol% MWCNT composite was found to be ~99.62%. SPS results in samples with a homogeneous microstructure and higher density. Due to the short sintering time, SPS also restricts grain growth resulting in a finer grain size. The relative density of conventionally sintered Al$_2$O$_3$–0.2 vol% MWCNT composites shows a slight decrease (~83.86–88.01%) with respect to the pure Al$_2$O$_3$ samples (~86.90–89.44%). Beyond the loading level of 0.2 vol% MWCNTs, the relative density of Al$_2$O$_3$–MWCNT composites was found to be higher than that of pure Al$_2$O$_3$ samples. The higher relative densities of Al$_2$O$_3$–MWCNT composites as compared to monolithic Al$_2$O$_3$ suggest that the MWCNTs uniformly filled the pores between the Al$_2$O$_3$ grains leading to better densification. The addition of 5 vol% MWCNTs to the Al$_2$O$_3$ matrix led to deterioration of the relative density of Al$_2$O$_3$–5 vol% MWCNT composites due to an agglomeration of MWCNTs at the Al$_2$O$_3$ grain boundaries. The relative density of conventionally sintered Al$_2$O$_3$–5 vol% MWCNT composites was found to be in the range of ~86.34–88.08%, whereas the relative density of SPSed Al$_2$O$_3$–5 vol% MWCNT composites was found to be ~99.55% [32].

Figure 15 shows the variations in relative density of Al$_2$O$_3$–MWCNT composites developed via different sintering routes.

The hardness of a pure Al$_2$O$_3$ sample developed by sintering at 1650°C for 3 h was found to be ~3.08 GPa. On the other hand, an SPSed pure Al$_2$O$_3$ sample showed a hardness of ~5.43 GPa. A slight drop in the hardness values of Al$_2$O$_3$–MWCNT composites was observed at a very low loading level of 0.2 vol% of MWCNT in the case of the conventionally sintered composites. A similar drop in the relative density of conventionally sintered Al$_2$O$_3$–MWCNT composites was also observed at a loading level of 0.2 vol% of MWCNT (Figure 15). This drop in hardness was not observed for SPSed Al$_2$O$_3$–MWCNT composites as compared to monolithic Al$_2$O$_3$.

Figure 16 shows the variations in hardness with the loading level of MWCNTs in Al$_2$O$_3$–MWCNT composites developed under different sintering conditions.

Figure 15. Variations in relative density of Al$_2$O$_3$–MWCNT composites developed via different sintering routes.

Figure 16. Variations in hardness of Al$_2$O$_3$–MWCNT composites developed via different sintering routes.
MWCNT composites. It is noteworthy that in the case of conventionally sintered composites, the hardness of all the composites was higher as compared to pure \( \text{Al}_2\text{O}_3 \) samples except for \( \text{Al}_2\text{O}_3-0.2 \text{ vol\%} \) MWCNT composites, whereas in the case of SPSed composites, this variation was not observed. The addition of MWCNTs up to 3 vol\% results in an increase in the hardness of \( \text{Al}_2\text{O}_3-\text{MWCNT} \) composites. The highest hardness was observed in the case of \( \text{Al}_2\text{O}_3-3 \text{ vol\%} \) MWCNT composites irrespective of the sintering technique adopted. The hardness of conventionally sintered \( \text{Al}_2\text{O}_3-3 \text{ vol\%} \) MWCNT composites developed by conventional sintering at 1650°C for 3 h was found to be \( \sim 4.109 \) GPa, whereas SPSed \( \text{Al}_2\text{O}_3-3 \text{ vol\%} \) MWCNT composite showed a hardness value of \( \sim 8.38 \) GPa. A drop in the hardness of the composites was observed when the concentration of MWCNTs was increased to 5 vol\%, which can be attributed to agglomeration of the nanofiller in the \( \text{Al}_2\text{O}_3 \) matrix. MWCNTs tend to agglomerate due to their high aspect ratio and strong van der Waals interactions, leading to poor densification of the composites and ultimately decreasing the hardness value. The addition of an optimum loading of 3 vol\% MWCNTs results in homogeneous distribution of MWCNTs in the \( \text{Al}_2\text{O}_3 \) matrix, which effectively restricts grain growth by grain boundary pinning. MWCNTs present around the grain boundaries can effectively reduce the atomic diffusion coefficient and prevent grain growth during sintering. A finer \( \text{Al}_2\text{O}_3 \) grain size results in higher hardness of the composites. The grain refinement effect of MWCNTs is also evident from the XRD plots of \( \text{Al}_2\text{O}_3-\text{MWCNT} \) composites in Figure 11 [33].

The tribological properties of \( \text{Al}_2\text{O}_3-\text{MWCNT} \) composites were investigated using a ball-on-plate tribometer. Figure 17 shows the wear rate of various \( \text{Al}_2\text{O}_3-\text{MWCNT} \) composites and clearly suggests that the variations in wear rate of the \( \text{Al}_2\text{O}_3-\text{MWCNT} \) composites follow a similar trend, irrespective of the sintering technique adopted. The wear rate of conventionally sintered \( \text{Al}_2\text{O}_3-\text{MWCNT} \) composites decreases continuously as the concentration of MWCNTs is increased up to 3 vol\%. The improved wear behavior of \( \text{Al}_2\text{O}_3-\text{MWCNT} \) composites as compared to monolithic \( \text{Al}_2\text{O}_3 \) is due to a protective triofilm formed on the wear track by MWCNTs, which provides the composites with effective wear resistance [34]. With the addition of MWCNTs above 3 vol\%, however, the wear rate shows a sudden increase due to heterogeneous agglomeration and clustering of MWCNTs in the sintered composite. In the case of conventionally sintered composites, moreover, the wear rate was found to be dependent on the sintering duration. \( \text{Al}_2\text{O}_3-\text{MWCNT} \) composites sintered at 1650°C for 1 h show a relatively higher wear rate, whereas composites sintered at the same temperature for 3 h show a relatively lower wear rate. This can be attributed to a higher level of densification in the case of the composites sintered for 3 h. SPSed \( \text{Al}_2\text{O}_3-\text{MWCNT} \) composites show a much lower wear rate as compared to conventionally sintered composites. However, the trend in the variation of wear rate with respect to the loading level of MWCNTs is similar to that of conventionally sintered composites [35].

The plots in Figure 18 show variations in wear depth with respect to time for various \( \text{Al}_2\text{O}_3-\text{MWCNT} \) composites. For conventionally sintered composites, it is evident from Figure 18(a–c) that the wear depth of \( \text{Al}_2\text{O}_3-\text{MWCNT} \) composites decreases with increase in the sintering duration. The minimum wear depth was observed for both conventionally sintered and SPSed \( \text{Al}_2\text{O}_3-3 \text{ vol\%} \) MWCNT composites. The plots suggest that the wear resistance of \( \text{Al}_2\text{O}_3-\text{MWCNT} \) composites improves significantly when MWCNT is introduced into the \( \text{Al}_2\text{O}_3 \) matrix up to a low loading level of 3 vol\%. A continuous improvement in the wear resistance of the composites with the addition of up to 3 vol\% MWCNTs can be seen from the plots in Figure 18(a–d). This increase in wear resistance can be ascribed to the lubricating behavior of the MWCNTs. At above the optimum loading level of 3 vol\% MWCNT in the \( \text{Al}_2\text{O}_3 \) matrix, however, the wear behavior of \( \text{Al}_2\text{O}_3-\text{MWCNT} \) composites
deteriorates. Al₂O₃–5 vol% MWCNT composites show the least wear resistance among all the Al₂O₃–MWCNT composites irrespective of the sintering route employed for their fabrication, a result that can be ascribed to the heterogeneous distribution and agglomeration of MWCNTs in the Al₂O₃ matrix. The higher wear depth observed for the monolithic Al₂O₃ sample corresponds to the removal of rough surface asperities due to its comparatively lower degree of densification and lubricity [36].

The SEM images in Figure 19 show the wear tracks of sintered pure Al₂O₃ and Al₂O₃–MWCNT composites. It is evident from the images that the width of the wear tracks is significantly reduced by increasing the sintering duration from 1 to 3 h. Composites sintered for 3 h display relatively smoother wear tracks, moreover, with hardly any noticeable grain pull-out as compared to composites sintered for 1 h. However, a large area of grain pull-out and severe damage to the wear surfaces, with traces of wear grooves and large residual wear debris on the wear tracks, can be observed for Al₂O₃–MWCNT composites sintered for 1 h (Figure 19(a,d,g,j,m)). When the MWCNT content is increased from 0.5 to 5 vol% in the Al₂O₃ matrix, abrasive sliding wear occurs resulting in a greater amount of Al₂O₃ grain pull-out. The width of the wear tracks decreased with increase in the sintering duration of the composites from 1 to 3 h, although the sintering temperature did not vary. For both 1 and 3 h sintered composites, a minimum wear track width is observed in the case of Al₂O₃–3 vol% MWCNT composites. The lower tangential frictional force between the composite surface of the wear track and the ball reduced the grain pull-out due to the formation of a protective tribofilm by the MWCNTs. MWCNTs embedded in the unpolished surfaces of the composites are dislodged and scattered on the wear track during the wear test to form a protective lubricating tribofilm. Moreover, the rolling effect of MWCNTs on the reduction of abrasion and wear rates cannot be ignored. MWCNTs also contribute to bridging the grains to protect against crack propagation during micro-chipping and grain pull-out for improving the wear resistance of the composites [37]. In the SPSed samples, the width of the wear tracks decreases with increase in the MWCNT content in the Al₂O₃ matrix due to the shorter sintering duration of SPS. The MWCNTs remain well preserved and assist in the effective lubrication of the Al₂O₃ matrix, which results in an overall improvement of the wear resistance of the composites.

Figure 20(a,b) show SEM images of wear debris obtained from the wear tracks of conventionally
sintered Al₂O₃–3 vol% MWCNT composites developed by conventional sintering at 1650°C for 2 and 3 h, respectively. It is clear from the SEM images that the sintering duration plays an important role in the conservation of MWCNTs in the Al₂O₃ matrix, since the wear debris collected from the 3-h sintered composite shows mostly Al₂O₃ particles with a negligible accumulation of MWCNTs. Longer sintering duration leads to better densification of the composites, making pull-out of MWCNTs difficult during the sliding wear test. This is also confirmed by the variations in wear rate in Figure 17 and the variations in wear depth in Figure 18. Both fine Al₂O₃ particles and MWCNTs sticking to Al₂O₃ particles can be clearly seen in the wear debris of the Al₂O₃–3 vol% MWCNT composite sintered at 1650°C for 2 h in Figure 20(a). The weakly bonded grain boundaries in the Al₂O₃ matrix chip off during the wear test, resulting in the removal and loss of a significant number of MWCNTs from the wear track. It should be noted that there was only a minor difference in the weight of the composites after the wear test, which is supported by the fact that only a very small amount of wear debris was collected after the test. Large clusters of Al₂O₃ particles can be seen in the SEM image of the wear debris of the SPSed Al₂O₃–3 vol% MWCNT composite in Figure 20(c). A large number of faceted Al₂O₃ grains can be seen in the SEM image in Figure 20(d). However, MWCNTs are not found in the wear debris of the SPSed Al₂O₃–3 vol% MWCNT composite. This is due to the higher level of densification obtained for SPSed composites, making pull-out of MWCNTs difficult [38].

The variations in fracture toughness values (K<sub>IC</sub>), determined using the notch indentation fracture toughness method for various sintered Al₂O₃–MWCNT composites, are shown in Figure 21. In the case of pure Al₂O₃ samples conventionally sintered at 1650°C for periods of 1, 2 and 3 h, toughness values in the range of ~2.6–2.8 MPa m<sup>1/2</sup> were obtained. There was a slight increase in the fracture toughness of pure Al₂O₃ when the sintering time was varied from 1 to 3 h, with the sintering temperature unchanged at 1650°C. The fracture toughness of Al₂O₃–MWCNT composites increased with the addition of MWCNTs and, however, achieved a maximum value of ~3.19 MPa m<sup>1/2</sup> in the case of Al₂O₃–0.8 vol% MWCNT composite conventionally sintered at 1650°C for a duration of 3 h. It should be noted that an optimum value for improvement in fracture
toughness was also observed for Al$_2$O$_3$–0.8 vol% MWCNT composites when conventionally sintered for 1 and 2 h. In all three cases, a loading level of 0.8 vol% of MWCNTs in the Al$_2$O$_3$ matrix provided the maximum value of fracture toughness, irrespective of the sintering duration. The holding time during sintering plays a great role in improving fracture toughness, as shown by the increase of ~7.4% in the toughness value of an Al$_2$O$_3$–0.8 vol% MWCNT composite developed by conventional sintering at 1650°C for 3 h as compared to that of an Al$_2$O$_3$–0.8 vol% MWCNT composite sintered at 1650°C for 1 h. Also, the incorporation of MWCNTs into the Al$_2$O$_3$ matrix significantly increased the fracture toughness of monolithic Al$_2$O$_3$ by ~12% when the loading level of MWCNTs was as low as 0.8 vol% at a sintering temperature of 1650°C and a holding time of 3 h. For SPSed composites, the highest fracture toughness of ~3.85 MPa m$^{1/2}$ was also observed in the case of Al$_2$O$_3$–0.8 vol% MWCNT composite. The improvement in fracture toughness can be ascribed to such prominent toughening mechanisms as crack bridging, crack blunting, crack deflection and MWCNT pull-out. The fracture toughness of the composites was found to depreciate with the addition of MWCNTs beyond 0.8 vol% due to the agglomeration of MWCNTs in the Al$_2$O$_3$ matrix. With increase in the loading level of MWCNTs in the Al$_2$O$_3$ matrix, the MWCNTs overlap, entangle and form complex clusters which weaken the grain boundaries. When the concentration of MWCNTs is increased, it results in the formation of an interlinked web-like structure of long nanotubes that weakens the nanofiller–matrix interface [39].

To investigate the various toughening mechanisms, the fractured surfaces of conventionally sintered
and SPSed Al₂O₃–MWCNT composites were observed under SEM. The SEM images in Figure 22 clearly indicate that crack bridging by MWCNTs is the main toughening mechanism of the Al₂O₃–MWCNT composites. When MWCNTs embedded in Al₂O₃–MWCNT composites encounter a crack, they bridge the crack wake and effectively obstruct its propagation. The pull-out of MWCNTs also contributes to toughening of the composites. Both MWCNT pull-out and crack bridging by the MWCNTs can be seen in the SEM images in Figure 22. The high aspect ratio of MWCNTs leads to a longer crack-wake bridging zone and improves the toughness of the composites. During crack propagation, an initial uncoiling of MWCNTs occurs in the crack wake, and when the crack propagates further, the uncoiled MWCNTs stretch elastically, serving as stretched MWCNT bridges instead of conventional frictional pull-out bridges. The MWCNTs are responsible for the interfacial strengthening as they tend to bridge the grains due to their high aspect ratio and hence impede the crack propagation. During deformation, MWCNTs can absorb energy through their highly flexible elastic behavior and increase the fracture toughness [40]. Additionally, MWCNTs can act as pinning points to stop grain boundary movements occurring under stress. Thus, MWCNTs embedded in the grains pin the Al₂O₃ grains together and strengthen the grain boundaries. As a result, these MWCNT-strengthened grain boundaries lead to a changed fracture mode, from intergranular in pure Al₂O₃ to transgranular in Al₂O₃–MWCNT composites. The smaller diameter of MWCNTs allows them to become embedded in the grains during grain growth, and their elongated shape enables them to link various grains together in order to form bridges. The sliding of concentric tubes of MWCNTs allows them to extend to significantly longer than their original length without breaking. MWCNTs can be stretched to a great extent before disintegrating during crack propagation and hence contribute to the bridging effect and toughening mechanism [41].

4. Conclusions

The effects of various sintering parameters such as sintering temperature, dwell time, sintering pressure and variations in nanofiller concentrations were analyzed for various conventionally sintered and SPSed Al₂O₃–MWCNT composites. It was found that addition of MWCNTs at significantly lower loading levels of up to 3 vol% remarkably enhances the mechanical and tribological properties of Al₂O₃-based composites. However, any further addition of MWCNTs into the Al₂O₃ matrix leads to the formation of complex clusters and their agglomeration in the host matrix, with resulting deterioration of the properties of the composites. The major conclusions drawn from the present research work are as follows:

(1) Good-quality MWCNTs were synthesized at optimized conditions using the LPCVD technique. The synthesized MWCNTs comprised concentric cylindrical graphene layers with an interlayer spacing of 0.34 nm. The outer diameter of the MWCNTs was found to be ~12 nm and the inner diameter ~3.3 nm.

(2) It was observed that a homogeneous dispersion of MWCNTs is attainable only at low concentrations (<5 vol%) and that any higher loading level
of MWCNTs than the optimum value of 3 vol% leads to their severe agglomeration.

(3) The conventionally sintered composites were found to possess better mechanical properties when sintered for a longer dwell time of 3 h than for a short sintering duration of 1 h. However, SPSed composites exhibit superior mechanical properties as compared to all conventionally sintered composites.

(4) The highest relative density of Al$_2$O$_3$-based composites was observed at 3 vol% loading of MWCNTs. In the case of conventionally sintered composites, the relative density of Al$_2$O$_3$–3 vol% MWCNT composite was found to be ~94.45%, whereas for SPSed Al$_2$O$_3$–3 vol% MWCNT composite, it was observed to be ~99.62%.

(5) The maximum value of hardness in the case of conventionally sintered composites was observed for samples sintered at 1650°C for 3 h. The hardness of Al$_2$O$_3$–3 vol% MWCNT composite was found to be ~4.1 GPa. In the case of SPSed Al$_2$O$_3$–3 vol% MWCNT composite, the hardness value increased by ~50.72% and was observed to be ~8.32 GPa.

(6) A significant improvement in the wear resistance of both conventionally sintered and SPSed Al$_2$O$_3$–MWCNT composites were achieved by using MWCNTs as a nanofiller. The wear tracks of 3 h sintered composites were narrower than those of composites sintered for 1 h, in the case of conventionally sintered composites. Also, an increase in the MWCNT concentration up to 3 vol% in the Al$_2$O$_3$ matrix showed a decrease in the diameter of the wear tracks. The strong interfacial interaction between MWCNTs and the Al$_2$O$_3$ matrix due to the formation of a protective tribofilm improves the wear resistance of Al$_2$O$_3$–MWCNT composites.

(7) The maximum value of fracture toughness in Al$_2$O$_3$–MWCNT composites was observed at a loading level of 0.8 vol% of MWCNTs. For conventionally sintered Al$_2$O$_3$–0.8 vol% MWCNT composites, it was observed to be ~3.19 MPa m$^{1/2}$, whereas for SPSed Al$_2$O$_3$–0.8 vol% MWCNT composites, it was found to be ~3.85 MPa m$^{1/2}$. A decrease in the fracture toughness of composites was observed at above 0.8 vol% of MWCNTs in the Al$_2$O$_3$ matrix. Crack deflection, crack bridging, crack branching and MWCNTs pull-out were found to be the main toughening mechanisms.

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