CARBON NANOTUBES-REINFORCING MgO-DOPED Al_2O_3 NANOCOMPOSITES

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ABSTRACT

Carbon nanotubes (CNTs) are probably the strongest material ever known with outstanding, electrical and physical properties. It is postulated that by transferring these fabulous properties as reinforcements in inorganic matrices, a new class of nanocomposites will be generated to meet the requirements of advanced applications. During the fabrication of CNT-reinforced ceramic composites, eliminating the agglomeration of CNTs and achieving high sintered densities are two main challenges. Recent studies have shown that CNTs can help matrix grain refinement but increase the sintering temperature, thus becoming a new hurdle to achieve near theoretical density. In this study, homogenous dispersion of CNTs was achieved with the addition of surfactant, sodium dodicyle sulphate (SDS), combined with a subsequent incubation for 2 weeks in an aqueous solution. MgO was added to the matrix in order to reduce the sintering temperatures and grain size. The dry mixture was then either sintered pressureless or hot pressed. The resulting nanocomposites were appraised by combined techniques, such as SEM, XRD and micro hardness testing. SEM investigation showed that the CNTs were retained in the nanocomposite with a homogenous dispersion within the Al_2O_3 matrix. The addition of a very small quantity of MgO (300 and 600 ppm) resulted in the CNTs/Al_2O_3 nanocomposite achieving a maximum density of ~87% and ~98% of the theoretical density using pressureless sintering and hot pressing at 1600°C for 1 hr, respectively. MgO doped nanocomposite exhibited 14% higher hardness as compared to pressureless sintered undoped samples. The MgO-doped nanocomposite manufactured by hot pressing exhibited higher mechanical properties *i.e.* 11% increase in density and 12% increase in hardness as compared to those prepared by pressureless sintering. After the high temperature sintering, the CNTs not only maintained their original shape and structural characteristics but also exhibited a good interface connection with the Al_2O_3 matrix. MgO and CNTs were observed to cumulatively participate in producing nanocomposites with a uniform and fine grain structure.

1. INTRODUCTION

Among the recent discoveries in materials science, CNTs are the most interesting material that has attracted the attention of scientists and technologists to develop new materials for advanced applications [1]. Both single and multi-walled CNTs have

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excellent mechanical properties, with modulus of elasticity ~1TPa and high tensile strengths. The exceptional electrical, physical and mechanical properties of CNTs have attracted the attention of industrial and scientific organizations worldwide for potential applications in diverse devices such as field emission display panels, nano-devices, fuel cells and hydrogen storage [2].

Nanocomposite materials are the hottest topic in the world of material specially the concept to use the CNTs as a reinforcing agent in different types of organic and inorganic matrices such as polymers, metals and ceramics. In one such effort, carbon nanotubes were used to reinforce polymer matrix and the resulting composites showed higher mechanical properties than their unreinforced polymer matrix. The biggest challenge in ceramics-CNTs nanocomposite manufacturing is the homogenous dispersion of CNTs because nanotubes tend to agglomerate with each other due to the strong Van der Waals interactions [3]. In most cases, the addition of CNTs as reinforcements improved the fracture toughness but decreased the hardness and strength. The main causes of inferior quality of nanocomposites are CNTs agglomerations and weak interfaces between CNTs and the matrix. Achieving a homogenous dispersion of CNTs in ceramic oxides, with strong bonding between the nanotubes and matrix, represents rather more of a challenge than incorporating CNTs into a polymer. Our recent studies have shown that CNTs can help matrix grain refinement but increase the sintering temperature, thus becoming a new hurdle to achieve near theoretical density [4].

Among ceramics, alumina is one of the most widely used materials having high hardness, good oxidation resistance and chemical stability, however its fracture toughness makes it inadequate for certain applications. It is assumed that the addition of CNTs as a second phase can enhance the mechanical properties of alumina [5]. Others developed CNT/alumina composites using carbon nanotube contents up to 12.5wt% and a significant reinforcement effect was reported [6, 7]. 10 vol% CNTs were also incorporated in alumina by Zhan *et al.* [8], and the fracture toughness of the final composite was twice that of the fully densified but un-reinforced alumina. Another study showed high electrical conductivity of CNT/alumina composites [9]. Colloidal processing was adopted to disperse multi-walled CNTs into alumina powder homogenously [10], and subsequent hot-pressed led to a 10% increase in bending strength of the nanocomposite compared with unreinforced alumina. Wang *et al.* observed that the addition of 0-300 ppm MgO could significantly increase the sintering density of pressureless sintered alumina-5 vol.% SiC nanocomposites [11]. Additions of small amounts of MgO reduce the effective sintering temperature to nearly 1600°C and restrict the grain growth of alumina matrix [12,13].

Here we report the manufacturing of MgO doped Al_2O_3-2wt% MCNTs nanocomposite with pressureless and pressure-assisted sintering. The effects of the addition of small amounts (300 ppm & 600 ppm) of MgO and CNTs, i.e. on the mechanical properties and microstructure of nanocomposites, were studied.

2. EXPERIMENTAL PROCEDURE
2.1 SAMPLE PREPERATION
Hot pressing and pressureless sintering techniques were used to fabricate the alumina matrix nanocomposites reinforced with up to 2wt% of multi-walled CNTs. The CNTs having an outer diameter of ~40 nm (Tsinghua University, Beijing, China) were chemically modified with H_2SO_4-HNO_3 solution and then dispersed into an aqueous

solution containing a small quantity of sodium dodycle sulphate (SDS, Sigma-Aldrich, UK), a surfactant, with the help of sonication for 30 min using an ultrasonic probe (Sonic Processor D-100-20, Sonic system, UK). The CNT slurry was incubated for 2 weeks, in order to thoroughly adsorb the surfactant onto the CNT surfaces. Al_2O_3 nanopowder with mean size of ~40 nm (Sigma Aldrich, UK) was then added and sonicated again for 2 h. After drying, the mixture was compacted at a pressure of 800 MPa into 12 mm diameter tablets using Moor Hydraulic Press and subsequently sintered at 1600°C for 60 min under Ar in a tube furnace (Elite, UK). Unreinforced alumina tablets, without CNTs, were also fabricated using the same method. 300 or 600 ppm MgO of mean diameter of 25~30 nm (Sigma Aldrich, UK), was incorporated in all samples in order to promote sintering. Nanocomposites doped with 300 ppm MgO were also hot-pressed (University of Mining and Technology, China) under a pressure of 300 MPa at 1600°C for 60 min under an Ar atmosphere.

2.2 MATERIAL CHARACTERIZATION AND MECHANICAL TESTING

For hardness evaluation, the sintered nanocomposite samples were fractured and cold mounted. During cold mounting, the samples were vacuum infiltrated using epoxy resin. After mounting, the samples were first ground on diamond pads of 120 and 220 grit and then polished to 6 micron and 1 micron by using DP-Suspension on polishing cloths. Microhardness testing was carried out at 9.8 N loads for 15 sec (M-400 hardness tester, LECO, Japan). The diagonal length of the diamond indent was measured using the attached microscope, converted to Vickers hardness number (HV) and further converted to GPa. Structural features of fractured samples were assessed by scanning electron microscopy (SEM, PHILIPS XL30, operated at 20 kV) and images were acquired using secondary electron (SE) signals. Prior to SEM observation, the samples were gold coated for 2 min. A Siemens D500 X-ray diffractometer with CuK_α radiation was applied at scan rate of 0.025θ/sec to identify the crystalline phases present in the nanocomposites, with the assistance of a computer software. (DIFFRAC^{plus} by Bruker Advanced X-ray Solutions). Densities of the sintered samples were measured by Archimedes method in distilled water, and the relative density was calculated by dividing the apparent density by theoretical density

3. RESULTS AND DISCUSSION

Achieving a homogenous dispersion of CNTs within the matrix is a major challenge to manufacture CNTs reinforced nanocomposites with superior mechanical properties. CNTs have the tendency to agglomerate, forming clusters and acting as impurities in nanocomposites consequently hurdling the interconnection with the matrix. In this viewpoint, the homogenous dispersion of CNTs in the matrix may have vital impact on the mechanical properties of the nanocomposites. The dispersion behaviour of CNTs in aqueous solution was assessed in three stages as shown in Figure 1. CNTs tended to settle whenever trying to obtain a suspension due to their hydrophobic nature, poor wetting characteristics and difference in density, as shown in Figure 1(a). After the addition of a small quantity of surfactant (SDS), a partial dispersion of CNTs was achieved as shown in Figure 1(b), because the addition of SDS improved the dispersion capability of water by decreasing its surface tension. After 2 weeks of incubation reaction time during which it is believed to achieve surfactant proper adsorption onto the CNTs surface and display uniform suspension of CNT in water as shown in Figure 1(c). During adsorption, SDS molecules create an "envelope" on the CNT surfaces as

shown in Figure 1(d), and this envelope increases the steric hindrance between CNTs, which counteracts the Van der Waals interaction. Moreover, the sulfonic group in the surfactant (SDS), by adsorbing onto the CNT surfaces, changes the wetting properties and makes the CNTs hydrophilic [14].
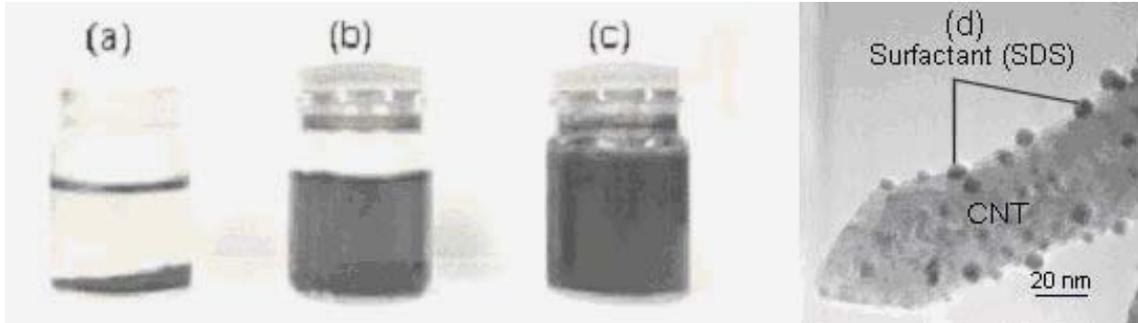

Figure 1: Suspended CNTs in an aqueous solution. (a) agglomerated CNTs, (b) partially suspended CNTs (c) homogenously suspended CNTs, (d) TEM image of SDS adsorbed on CNTs.
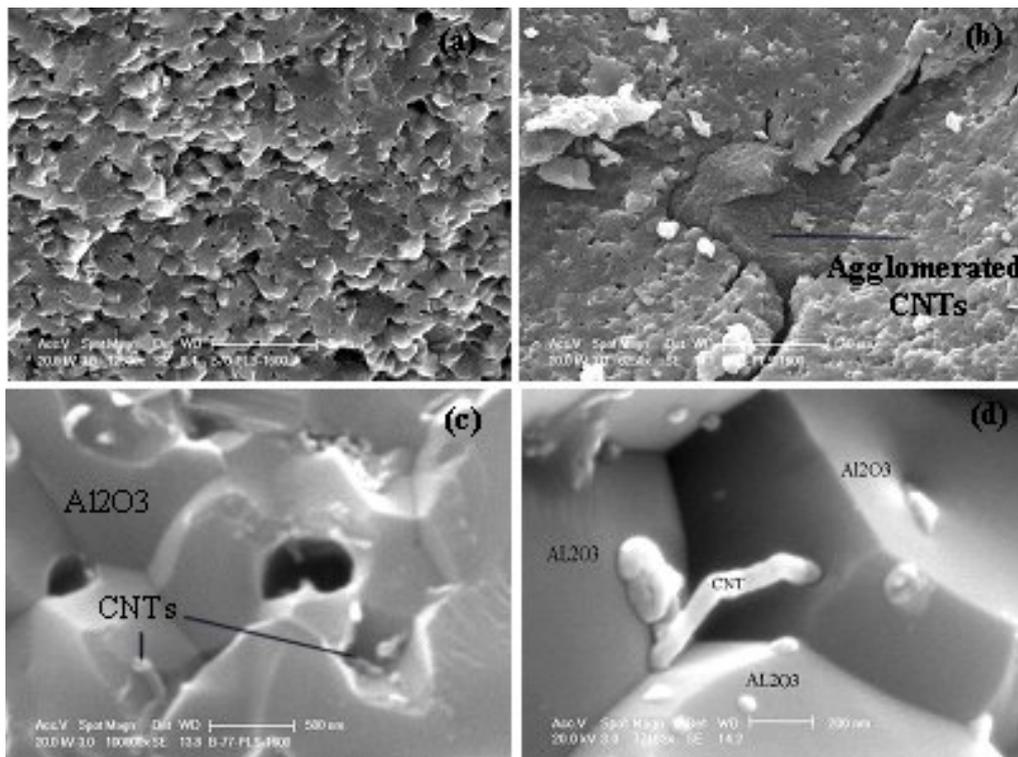

Figure 2: SEM images of MgO doped Al_2O_3 -2wt% CNTs nanocomposites (a) well-dispersed CNTs, (b) agglomerated CNTs (c) individually dispersed CNTs (d) a CNT bridging the Al_2O_3 grains.

The dispersion of CNTs in the alumina matrix was assessed by SEM examination of the fractured nanocomposite samples. Homogenous dispersion was achieved after an incubation period of 2 weeks after SDS was added to the CNT solution before mixing with the ceramic powders, as shown in Figure 2(a). Nanocomposites manufactured without the addition of SDS exhibited severe agglomeration as shown in Figure 2(b) in

which huge agglomerates of CNTs are clearly visible. Individually well-dispersed CNTs having good connection with the ceramic grains have been revealed at higher magnification in Figure 2(c). Homogenous CNT dispersion led to higher hardness whilst agglomeration resulted in lower hardness. The superior hardness is due to an enhanced load sharing by the homogenously dispersed CNTs which also confirmed good adhesion between CNTs and the matrix [15]. Furthermore, well-dispersed CNTs have individual interactions with the Al_2O_3 nanoparticles and can act as reinforcements by forming bridges between crack surfaces as shown in Figure 2(d), where a CNT firmly holds the alumina grains [16]. In other cases, when bundles/lumps of CNTs occurred, there was no interaction between the CNTs within the bundle and the matrix and the lumps acted as an impurity, without any reinforcing effect, resulting in mechanically weak nanocomposites.

Typical peaks from α-alumina were observed in the X-ray diffraction (XRD) patterns of MgO doped alumina-CNTs nanocomposite as shown in Figure 3. High crystallinity of the α-alumina phase suppressed the MgO and CNTs peaks due to their low contents in the nanocomposites, hence no CNT and MgO peaks were identified.
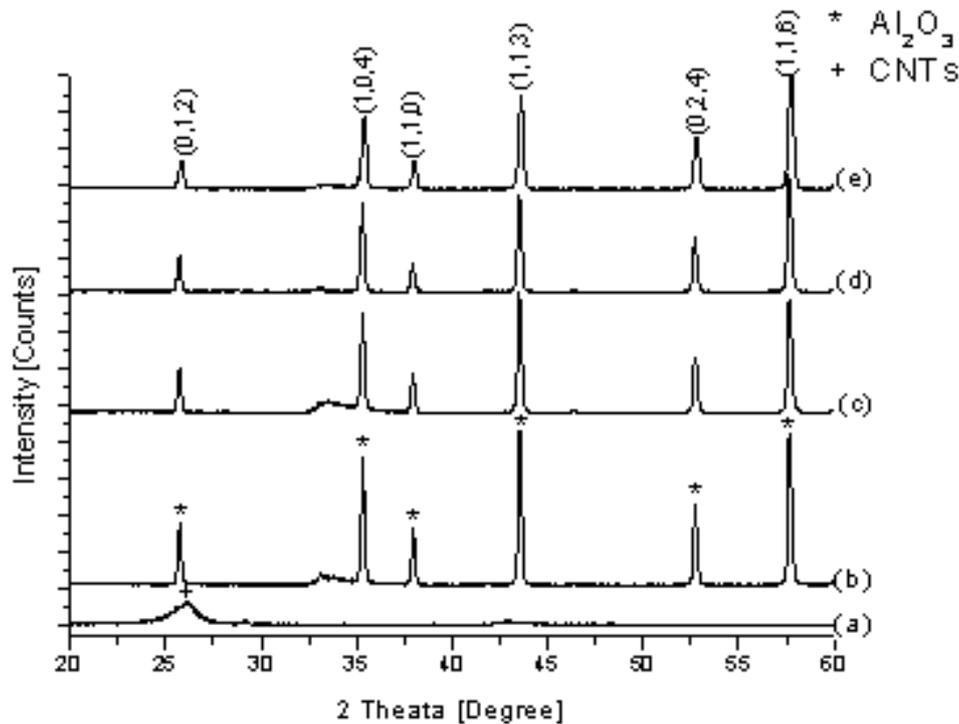

Figure 3: XRD Pattern of MgO doped Al_2O_3–CNTs nanocomposites, (a) CNTs, (b) Al_2O_3, (c) 300 ppm MgO-doped Al_2O_3, (d) 600 ppm MgO-doped Al_2O_3, and (e) 300 ppm MgO-doped Al_2O_3-2wt% CNTs nanocomposite.

Effects of MgO addition on the density of Al_2O_3 are shown in Figure 4-1(A) and it can be seen that the addition of a small amount (300 ppm and 600 ppm) of MgO improved by 2% and 4% of the density of the unreinforced Al_2O_3, respectively. It has been reported that the addition of MgO at ppm level significantly reduced the sintering temperature and grain size and increased the sintered density of a pressureless-sintered alumina [17-18]. The final properties of Al_2O_3 depend on the microstructure developed during sintering; moreover undoped alumina is very difficult to sinter to theoretical

density. The major factor that hinders the densification is abnormal grain growth and pore detachment from the grain boundaries during boundary migration, which effectively leaves the pores permanently trapped inside the grains [19]. Small amounts of dopant, such as MgO, can improve the densification and microstructure development of alumina [20].
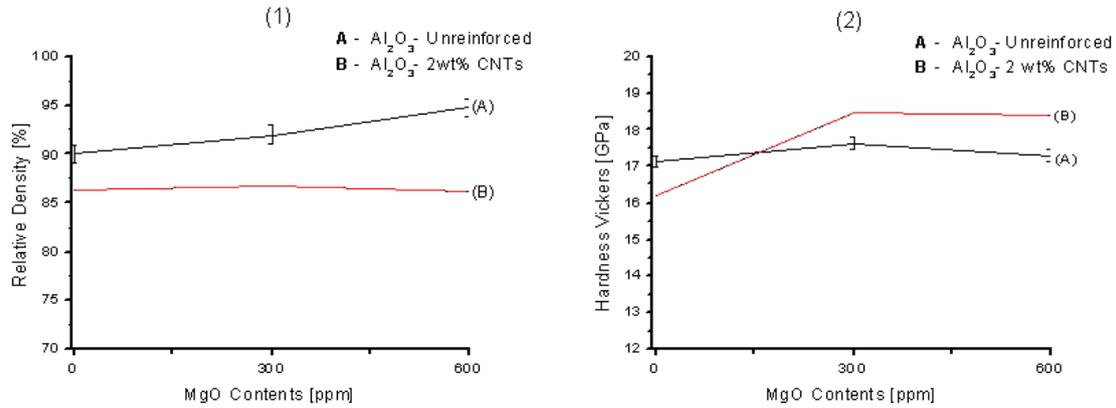

Figure 4: Effect of MgO concentrations on (1) density and (2) hardness of Al_2O_3-CNTs nanocomposites manufactured by pressureless sintering.

Dopants can also alter the boundary, lattice and surface diffusivities, leading to a change in boundary and pore mobilities. They can create drag forces on boundary motion by segregating to grain boundaries, and when segregation increases, they can pin the grain boundaries, thus inhibiting the grain growth. If the concentration of dopant is increased at the grain boundary, it becomes oversaturated and a new phase is formed [21]. However, negligible improvement in the density of CNTs-Al_2O_3 nanocomposites was observed in this context, as shown in Figure 4-1(B). This might be associated with the addition of CNTs in Al_2O_3, because addition of a second phase such as CNTs increased the sintering temperatures of the nanocomposites and hurdle to achieve near theoretical density using pressureless sintering [22]. 300 ppm MgO-doped Al_2O_3 and CNTs-Al_2O_3 nanocomposites exhibited higher hardness as compared to undoped Al_2O_3, however further increase in MgO contents, *i.e.* 600 ppm, had no significant effect on hardness as shown in Figures 4-2. The 14% increase in hardness of CNTs-Al_2O_3 nanocomposites with 300 ppm MgO addition is possibly due to the lowered sintering temperature during presureless sintering and the firm attachment of CNTs to the Al_2O_3 grains which resists cracking by forming bridges between grains.
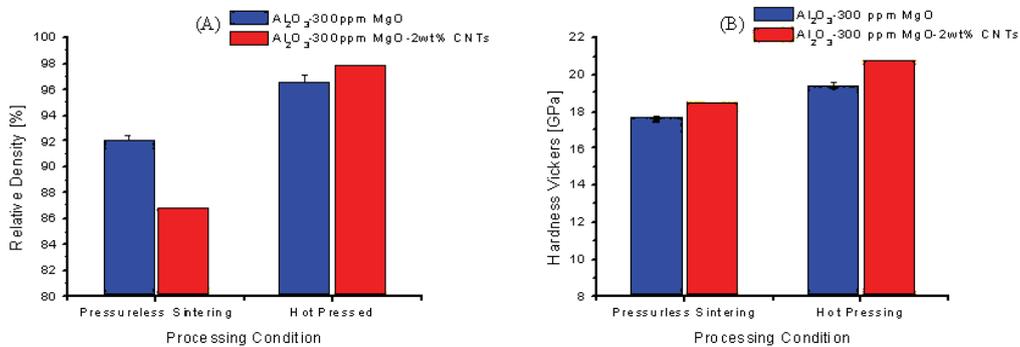

Figure 5: Effect of processing condition on (A) density and (B) hardness of 300ppm MgO doped Al_2O_3 -CNTs nanocomposites.

Pressure-assisted sintering improved the density and hardness of both the unreinforced (by 5% and 11%) and the CNT-reinforced Al_2O_3 (by 11% and 12%) samples, as compared to pressureless sintering, as shown in Figure 5. During hot pressing, the high density of plain Al_2O_3 is due to accelerated densification which can be attributed to an increased stress due to the externally applied pressure, which consolidates the grain to a higher density [23]. The increase in density of $CNTs$-Al_2O_3 nanocomposites is, possibly, due to the combined effect of applied pressures and CNTs because CNTs reduce the grain size by pinning the grain boundaries and develop nanocomposites structure with fine grains. On the basis of the hardness results, it can be predicted that the pressure assistance during high temperature sintering process also increased the interaction between the CNTs and matrix which is responsible for good cohesion between them by forming strong interface.
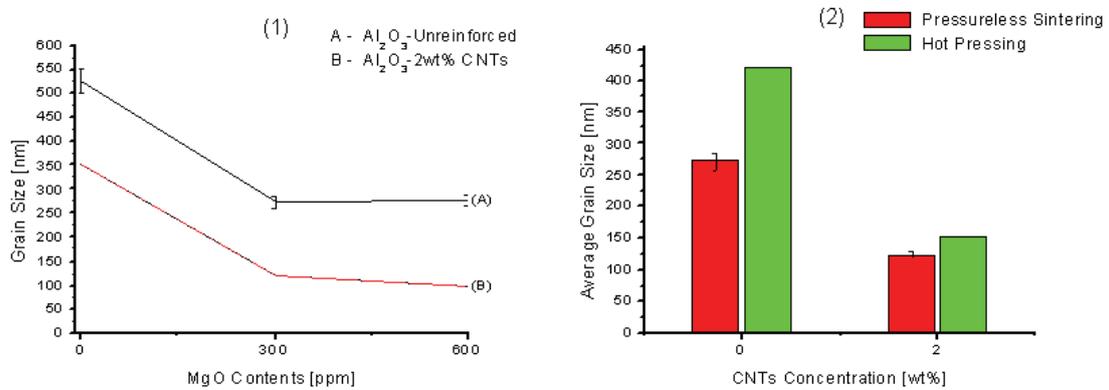

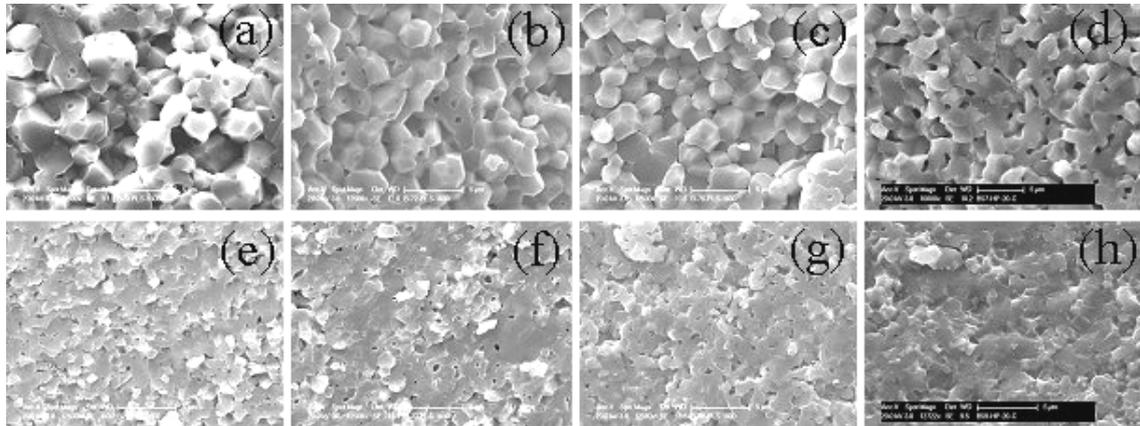Figure 6: Effect of (1) MgO and (2) processing condition on the grain size of Al_2O_3 and Al_2O_3-CNTs nanocomposites.

Figure 7: MgO Doped Al_2O_3-CNTs nanocomposites sintered at 1600°C for 1 hr in argon (a) undoped Al_2O_3, (b) 300 ppm MgO doped Al_2O_3, (c) 600 ppm MgO doped Al_2O_3, (d) 300 ppm MgO doped Al_2O_3 hot pressed at 300 MPa, (e) undoped Al_2O_3-2wt% CNTs, (f) 300 ppm MgO doped Al_2O_3-2wt% CNTs, (g) 600 ppm MgO doped Al_2O_3-2wt% CNTs, and (h) 300 ppm MgO doped Al_2O_3-2wt% CNTs hot pressed at 300 MPa.

Figure 6-1 shows that the addition of 300 ppm MgO decreased the grain sizes of the CNT-free Al_2O_3 samples, however no apparent improvement was observed with the

addition of 600 ppm MgO. SEM images of fractured samples, Figure 7(a), revealed uneven grain growth in the undoped Al_2O_3, but MgO additives helped in forming finer and more uniform grains, as shown in Figures 7(b) and 7(c). In the case of CNTs-reinforced Al_2O_3, CNTs acted as a grain refining agent, already explained above, during the composite sintering as shown in Figure 7(e), where an undoped Al_2O_3-CNTs nanocomposite exhibited a fine grain structure when compared with undoped plain Al_2O_3. However, further difference in the grain size of the Al_2O_3-CNTs nanocomposites doped with different contents of MgO could not be identified as shown in Figures 7(f) and 7(g).

Hot pressed samples revealed interesting microstructural features. 300 ppm MgO doped Al_2O_3 and Al_2O_3-CNTs nanocomposites exhibited slightly larger grain sizes when compared to those manufactured by pressureless sintering as shown in Figures 6-2. The development of large grains during hot pressing can be associated with the drag forces on boundary motion because applied pressures during sintering increased the densification rate resulting in the reduction of drag forces during the sintering process which in turn generate large grain structure with homogenous in size, as shown in 7(d) and 7(h), consequently hardness increased [24]. Hence, it is possible that the addition of MgO had no significant effect on the grain refinement but may have altered the sintering characteristics of Al_2O_3 in the composites. It was also noted that under Ar protection, it is very difficult to achieve 100% of the theoretical density with pressureless sintering of the nanocomposites due to O_2 losses from alumina at high temperatures [25].

4. CONCLUSIONS

Uniform dispersion of CNTs during the manufacturing of CNT-reinforced MgO-doped alumina nanocomposites has been achieved. SDS surfactant, and an incubation time of two weeks of the CNTs-water slurry before mixing with the ceramic nanopowders, played an important part in achieving the uniform dispersion of CNTs. The addition of 300 ppm MgO increased the density *i.e.* 2% of unreinforced Al_2O_3 but not the Al_2O_3-CNTs nanocomposites. However, MgO as a dopant increased the mechanical properties, *i.e.* 14% higher hardness, of the Al_2O_3-CNTs nanocomposites prepared by pressureless sintering. Nanocomposites with 11% improved density and superior mechanical properties, in term of 12% higher hardness, were successfully fabricated with the help of hot pressing. Pressure-assisted sintering had an important effect on the final microstructure and properties of the Al_2O_3-CNTs nanocomposites pressures, applied during high temperature sintering lead to higher density and hardness as compared to unreinforced ones.

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