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Improved densification and mechanical properties of spark plasma sintered carbon nanotube reinforced alumina ceramics

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HIGHLIGHTS

- Improved densification of insulating Al_2O_3 through CNT addition and SPS.
- Process schematic and description on probable current conduction paths during SPS.
- *W-H* analyses to reinforce the positive effect of CNT towards higher densification.
- Improved mechanical properties of dense nanocomposites.
- Enhanced tribological performance of nanocomposites against diamond indenter.

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ABSTRACT

Dense magnesium oxide (MgO) doped multiwalled carbon nanotube (MWCNT) reinforced alumina (Al_2O_3) nanocomposites were fabricated using spark plasma sintering (SPS). Sintered nanocomposites possessed refined microstructure due to the presence of uniformly dispersed CNTs and ability of MgO to increase densification rate before onset of abnormal grain growth. *Williamson-Hall* analyses of XRD patterns indicated that matrix crystallite size (L_C) and lattice micro-strain (ε_C) of the nanocomposites decreased by ~40% and >30%, respectively, than those of pure Al_2O_3 ($L_C \approx 75$ nm, $\varepsilon_C = 1.54 \times 10^{-3}$). Present investigation also depicted the suitability of CNT addition in Al_2O_3 towards achieving higher density of nanocomposites using low temperature (1300 °C) SPS. Addition of CNT (especially, at ≥0.6 vol.%) in highly electrically insulating matrix established an electrical percolating network that helped in local heating of matrix particles during SPS and led to higher densification. The highest changes in indentation fracture toughness at 1 kgf and wear rate at 20N normal load were obtained at only 0.6 vol.% MWCNT loading which were >22% higher and 35% lower, respectively, compared to pure Al_2O_3.

1. Introduction

The discovery of the outstanding allotrope of sp^2 hybridized carbon i.e. CNT has undeniably established a new horizon for futuristic high-performance materials [1–4]. Not only as individual but also as filler in ceramics, polymers and metals, CNT is gradually proving its suitability over many existing materials [3–9]. However, fabrication of CNT/ceramic nanocomposites with the ability to offer enhanced structural performance over parent matrices requires special attention to overcome certain processing limitations. These are mainly improper dispersion of CNTs in matrix, presence of CNT agglomerates without any reinforcing effect, structural collapse of CNT during high temperature sintering, poor densification of matrix phase due to presence of CNTs at grain-boundary regions etc. [7,10–13]. Structural CNT/Al_2O_3 nanocomposite is not an exception in this regard and analogous to other CNT/ceramic nanocomposites, global R&D activities are still continuing to trace out effective routes to overcome such limitations for fabricating CNT/Al_2O_3 nanocomposites having improved structural performance over pure Al_2O_3 [14–19]. In general, incorporation of CNT in Al_2O_3 usually retards densification kinetics and produced porous and/or segregated microstructures having inferior performance compared to pure Al_2O_3 [7,10]. The level of such sintering hindrance found to

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be increased with increasing CNT loading [18,20]. In this work, an attempt has been made to fabricate dense 0.15–2.4 vol.% MWCNT reinforced Al_2O_3 nanocomposites through local heating of matrix particles utilizing the exceptional electrical conductivity of CNT during SPS. In addition, specimens were doped also with 0.5 wt.% MgO to extend intermediate stage of sintering, promote densification rate and inhibit abnormal grain growth [21,22]. Finally, to access the nature of changes in various properties, the fabricated nanocomposites as well as a control have been evaluated in terms of bulk density (*BD*), apparent porosity (*AP*), microstructure, matrix L_C and ε_C values, electrical conductivity, *Vickers* hardness (*HV*), indentation fracture toughness (K_{IC}) and unlubricated linear scratch resistance.

2. Experimental

2.1. Raw materials

Polycrystalline Al_2O_3 powder (*A-16-SG*, purity: 99.8 wt.%, d_{50} = 0.5 μm, *M/s Almatis Alumina Pvt. Ltd., India*) was used as the source for the matrix. MWCNT used in this study was procured from *M/s Shenzhen Nano-Tech Port, China* having purity >95 wt.%, outer diameter 60–100 nm and length 5–15 μm. MgO powder (*M/s Merck Specialties Pvt. Ltd., India*) was used as sintering additive to Al_2O_3.

2.2. Batch preparation and sintering

Appropriate quantity of pristine MWCNT was dispersed in isopropyl alcohol (IPA) for 1 h using a 250 W bath sonicator (*Micro Clean 109, M/s Oscar Ultrasonics Pvt. Ltd., India*). Attrition milling using IPA and Φ = 3 mm Al_2O_3 balls in a *PE-075* laboratory batch mill (*M/s Netzsch-Feinmahltechnik GmbH, Germany*) was carried out for another 3 h to properly mix the dispersed CNT slurry and requisite amount of Al_2O_3 and 0.5 wt.% MgO powders. The mixed slurry was then air dried at 70 °C for volatile removal and sieved through a 60 mesh BS screen and collected. Five different MWCNT/Al_2O_3 powder mixtures along with a pure Al_2O_3 batch were prepared following the above steps (Table 1). The powder mixtures were consolidated using a *HP-D-25* SPS furnace (*M/s FCT GmbH, Germany*) using graphite mould (Φ = 20 mm) at 1300 °C and 60 MPa uniaxial pressure with 10 min dwell under static Argon atmosphere (Fig. 1).

2.3. Physical properties, microstructure and phase analyses

Bulk density (BD) and apparent porosity (AP) of sintered specimens were evaluated using *Archimedes* water immersion technique. Microstructures of polished and chemically etched specimens were viewed through a field-emission scanning electron microscope (FESEM: *Supra-35, VP-Carl Zeiss, Germany*). X-ray diffraction (XRD) patterns (2θ = 10 to 90°; step size = 0.05°) of consolidated specimens were recorded using *Bruker D8 Advance DA Vinci* XRD System. Beside phase detection, XRD patterns were also utilized to evaluate matrix L_C and ε_C values applying *Williamson-Hall* (*WH*) technique using the following equation [23]:

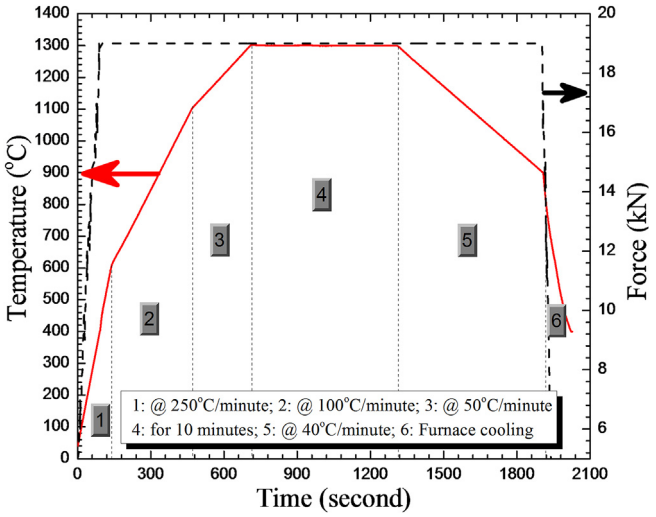

Fig. 1. The SPS schedule.

$$\beta \cos\theta = \frac{k\lambda}{L_C} + 4\varepsilon_C \sin\theta \quad (1)$$

where, β = integral breadth, θ = *Bragg* angle, *k* = *Scherrer's* constant; 0.9 and λ = 1.5406 Å.

2.4. Electrical property

DC electrical conductivity of powder batches were measured using cold isostatically pressed (150 MPa for 1 min) square blocks of ~(28 × 28 × 11) mm^3 dimension. For a specific purpose, the pressed blocks were sintered using pressureless sintering (PLS) technique in a graphite resistance heating furnace *(1000-4560-FP20; M/s Thermal Technology LLC. USA)* at 1700 °C for 2 h under static Argon atmosphere (35–70 kPa). Prior to electrical characterization, thin conductive silver (Ag) layers were applied on two opposite faces of the sintered samples and cured at 150 °C in an air oven. For green samples, (28 × 28 × 1) mm^3 thin copper plates were used and gripped with the sample surface using non-conducting plastic clips. Finally, conductivity values of all the PLS-ed and SPS-ed specimens were measured by standard 2-probe method using a *2400 Sourcemeter, M/s Keithley Instrument Inc., USA*.

Table 1
Specimen id's, CNT and MgO concentration, theoretical and relative density values along with apparent porosity data of the studied specimens.

CNT loading (vol.%)	MgO content (wt.%)	T.D.[a] (g/cc)	SPS-ed specimens (1300 °C/60 MPa/10 min/Ar)			PLS-ed specimens (1700 °C/2 h/Ar)		
			Id	RD (%)	AP (vol.%)	Id	RD (%)	AP (vol.%)
0.00	0.5	3.968	*A0SP13*	97.06	0.38	*A0PL17*	98.03	0.30
0.15	0.5	3.965	*A0.15SP13*	97.79	0.39	*A0.15PL17*	97.60	0.60
0.30	0.5	3.961	*A0.3SP13*	98.18	0.43	*A0.3PL17*	96.95	0.75
0.60	0.5	3.955	*A0.6SP13*	99.35	0.47	*A0.6PL17*	95.32	1.53
1.20	0.5	3.942	*A1.2SP13*	98.57	0.82	*A1.2PL17*	95.13	2.79
2.40	0.5	3.916	*A2.4SP13*	97.59	1.31	*A2.4PL17*	91.93	5.92

[a] T.D. = Theoretical density; Calculated using '*Rule of Mixture*' and taking ρ_{Al2O3} = 3.970 g/cc; ρ_{MgO} = 3.581 g/cc; ρ_{MWCNT} = 1.775 g/cc.