



Towards High Temperature Applications of Carbon nanotubes (CNTs) [II]: Structural characterizations of CNTs reinforced Silica nanocomposite

Yusuf Tijjani
Department of Mechanical Engineering,
Faculty of Engineering, Bayero University, Kano
Kano State, Nigeria.

ABSTRACT

Functionalized carbon nanotubes/silica refractory ceramic nanocomposites (FCNTs/silica) were consolidated by pressureless sintering via conventional powder processing technique (CPPT). Ultra High-resolution scanning electron microscope with Electron diffraction X-ray spectroscopy (FESEM/EDX) and Raman spectra of 0, 1 and 4 wt. % FCNTs-silica nanocomposites, searching for CNTs after pressureless sintering process are presented. Also shown, are Field Emission Transmission Electron Microscope (FE-TEM) micrograph and typical morphology of Vickers' indented surface for the attempted micro-hardness testing. The CNTs have structurally survived the high temperature pressure less sintering. Furthermore, the surface contents some pores; this might be the reason for the obtained low density and high porosity of the nanocomposite. The Hardness and fracture toughness could not be determined by Vickers' indentation technique due to the porous nature of the FCNTs/silica surfaces and the absence of classical radial cracks.

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INTRODUCTION

The silica utilized for the fabrication of silica refractories appeared in the form of quartz; quartz is the only type of silica that is stable at atmospheric temperature, hence, all the un-combined silica in the earth's crust exists as quartz and is present in quartzite, canister, sand, flints, etc. Quartzite which contents the low-quartz modification (α -quartz) is the most used form of quartz employed for the production of silica refractories in most countries. This is achieved via conventional coarse ceramic manufacturing that involves preparation, shaping, drying and firing (Brunk, 2000). Due to its high aspect ratio, carbon nanotube has been referred to ideal filler for potential applications in electronic devices and structural components (Norizan et al., 2020). Conventional powder processing technique (CPPT) as applied to CNT-silica; involves the dispersion of CNT in a polar solvent, wet mixing with the silica, ultrasonication/ball milling, drying, crushing and sieving, and finally cold compaction and consolidation/densification to obtain sintered CNT-silica nanocomposite pellets (Subhani et al., 2013).

Carbon nanotubes has been recently added in the matrix of traditional/natural crystalline silica (quartzite) as filler/sintering-aid mineralizer processed through CPPT to confer improved physical, mechanical and functional properties (Tijjani et al., 2018; Tijjani et al., 2019; Tijjani and Nasir, 2019). The contention is whether the carbon nanotubes survived the high temperature pressureless sintering to enhance these properties or not. Thus, the present research revisits some of the definitive structural indicators.

EXPERIMENTAL PROCEDURE

Materials

Pristine Carbon nanotubes (Multiwalled, CVD-grown, > 98 % purity, 10 – 20 nm diameter, and 10 – 30 μ m length) were received from the Chengdu Organic Chemicals Co., Ltd, Chinese Academy of Sciences (Sichuan Sheng, China). As-mined Silica and clay both obtained from Gezawa quarry (Kano, Nigeria); the Silica has been purified, crushed, ground, and pulverized using crushers, ball mill, and pulverizer at National metallurgical development centre NMDC (Farar-gada, Jos,

Nigeria). CaO powder (ChemPur®, SYSTEM) was purchased from Classic Chemicals Sdn Bhd (Selangor, Malaysia).

PRODUCTION of FCNTS/SILICA NANOCOMPOSITE

The graded powdered silica with average particle size, $d(0.5) = 20.166 \mu\text{m}$, clay with size $< 75 \mu\text{m}$ and CaO powder were added to portion of the stable suspension of FCNTs as-prepared by Tijjani et al., 2018. These were thoroughly mixed, cold compacted, and sintered at 1450°C for 2 hours dwelling time, into sample pellets ($\varnothing 21 \text{ mm} \times 8 \text{ mm}$ height) via conventional powder processing technique in a similar procedure as described by Tijjani et al. (2018). The produced densified pellets are: 0 wt. % FCNTs + S (SC-0), 1 wt. % FCNTs + S (SC-1), and 4 wt. % FCNTs + S (SC-4) were subjected to structural characterizations. Where, S stands for silica plus sintering aids (CaO + clay) and C for functionalized CNTs.

Structural characterization

The microstructural characterizations of the nanocomposite were determined by Ultra High-resolution scanning electron microscope with Electron diffraction X-ray spectroscopy (FESEM/EDX, Nova NanoSEM 230), Field Emission Transmission Electron Microscope (FE-TEM, JEM-2100F, USA), Raman Spectroscopy (Alpha 300R, WITec), while the density and porosity of the nanocomposites were measured by Archimedes' method.

RESULTS AND DISCUSSION

Structural properties

Microstructural characterization

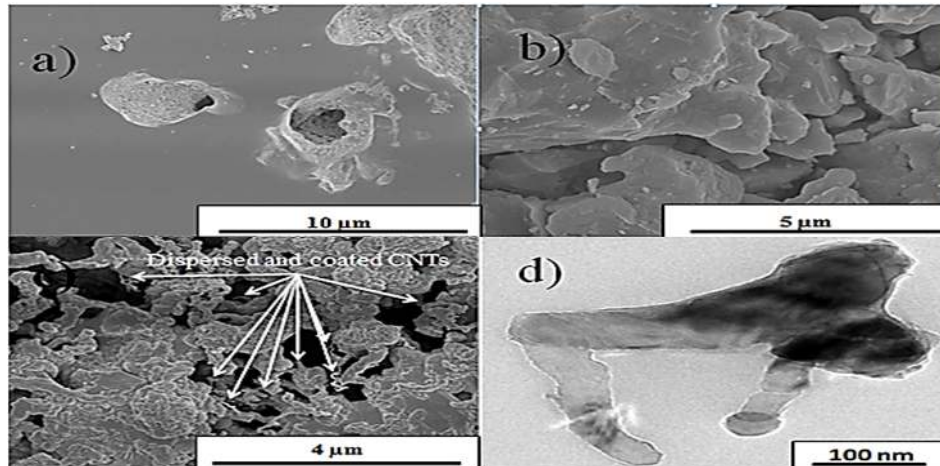


Figure 1: FESEM micrograph of a) SC-0 b) SC-1 c) SC-4 d) FE-TEM micrograph of SC-4

It has been reported that XRD is not an effective technique for detecting CNTs in ceramics, glass, and glass-ceramics composites (Boccaccini et al., 2005; Cha et al., 2005; Ye et al., 2006). Although some reports argued that it could be used for more than 5 wt. % CNTs content (Jiang & Gao, 2008), and some literature believed that the retention could be detected for sintering temperature up to 1200°C (Subhani et al., 2013). Thus, for the present study, only FESEM/EDX, FE-TEM and Raman spectroscopy were used to ascertain the presence and structural integrity of the CNTs after sintering.

FESEM/EDX/FE-TEM

The FESEM micrographs and EDX percentage compositions for SC-0, SC-1, and SC-4, searching for structurally surviving CNTs after pressureless sintering process are presented in Figure 1 and Table 1 respectively. By observing the FESEM micrographs in Figure 1 (b) for sample SC-1, there is no evidence of any carbonaceous material, whereas in Figure 1 (c) for SC-4, some dispersed and coated nanotubes resembled materials are sighted. Results from EDX of weight proportion of SC-1 and SC-4 revealed a respective carbon content of 6.61 wt. % and 9.14 wt. % as related to the free carbon SC-0. These further signify the possibility of the retention of carbon-based materials in SC-1 and SC-4. Finally, the FE-TEM image as shown in Figure 1 d, provides a definitive proof for the structural survival of CNTs in the nanocomposite bricks.

Table 1: EDX showing the elemental composition in sintered disk SC-0, SC-1 and SC-4

SC-0		SC-1		SC-4	
Element	Wt. %	Element	Wt. %	Element	Wt. %
O	53.12	O	50.07	O	46.59
Si	44.79	Si	40.53	Si	43.13
Ca	2.08	Ca	2.80	Ca	1.13
		C	6.61	C	9.14

Raman Spectra

The characteristic CNTs peaks at approximately 1300 cm⁻¹, 1580 cm⁻¹, and 2710 cm⁻¹ (Costa & Borowiak-Palen, 2009; Murphy et al., 2006) in SC-1 and 1376 cm⁻¹, 1598 cm⁻¹, and 2614 cm⁻¹ (Bokobza & Zhang, 2012; Tijjani et al., 2018) in SC-4 (Figure 2) for D, G, and G' bands respectively are clearly observed; providing additional proof for the structural survival of CNTs in the nanocomposite bricks.

densification with increased % FCNTs can be associated with the development of pores due to CNTs aggregation that may set in as the percentage of FCNTs increase (Bai & Xie, 2017; Jiang & Gao, 2008; Li & Liu, 2015; Subhani et al., 2013). More precisely, it is understood that some the nanotubes have been successfully coated with CaO (a compatible binder and mineralizer for silica and remarkable substrate for CNTs); these nanotubes survived the high sintering temperature as could be seen

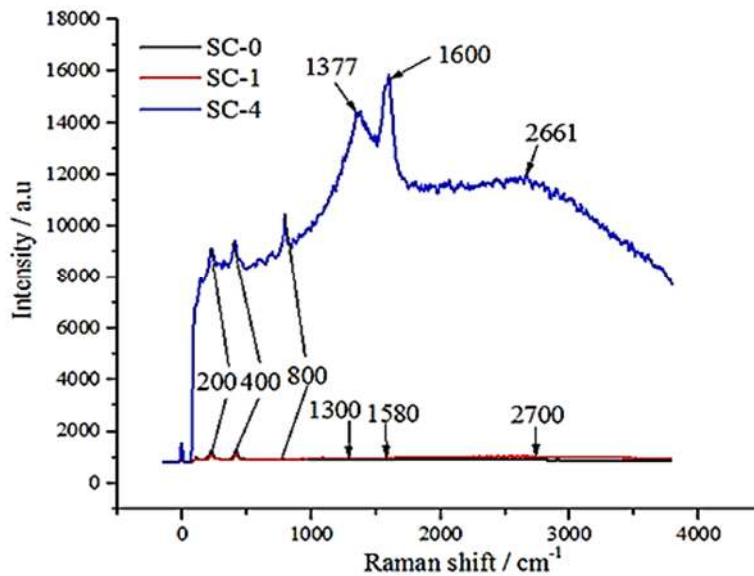


Figure 2: Raman spectra depicting SC-0, SC-1, and SC-4, the CNTs have structurally survived the pressureless sintering at 1450oC for 2 hours holding time in an argon atmosphere

Density and porosity

The effect of the addition of % FCNTs on the bulk density (BD) and apparent porosity (AP) of FCNTs/silica bricks is tabulated in Table 2. As the percentage of the nanotubes increase to 1 and 4 %, the bulk density reduces slightly and the apparent porosity increases. The negligible reduction in

dispersed in Figure 1 (c) for SC-4. Whereas, some of the CaO-uncoated nanotubes may tangle and join together by virtue of attraction due to the Van der Waals forces, thus, aggregating. These agglomerates may not be infiltrated by crystalline silica during the pressureless sintering, hence, lead to the development of pores (Figure 1 (c)). Fascinatingly, the coated nanotubes were observed aiming to fill the voids in Figure 1 (c).

Table 2: Influence of % CNTs on BD and AP of FCNTs/silica bricks

Samples	Wt. % FCNTs	BD (g/cm ³)	AP (%)
QC-0	0	1.74±0.00	32.62±0.02
QC-1	1	1.74±0.01	41.28±0.41
QC-4	4	1.72±0.00	52.45±0.44

Determination of Hardness and Toughness using Micro-Vickers-indentation Technique

An attempt has been made to determine the fracture toughness of the samples using Micro-Vickers-indentation and Antis' equation (Antis et al., 1981). Figure 3,

determination of toughness using the micro Vickers indentation technique is not valid for CNTs/silica nanocomposites. Though even if there is no issue with this method, it is generally considered as unreliable technique (Estili and Sakka, 2014; Quinn and Bradt, 2007).

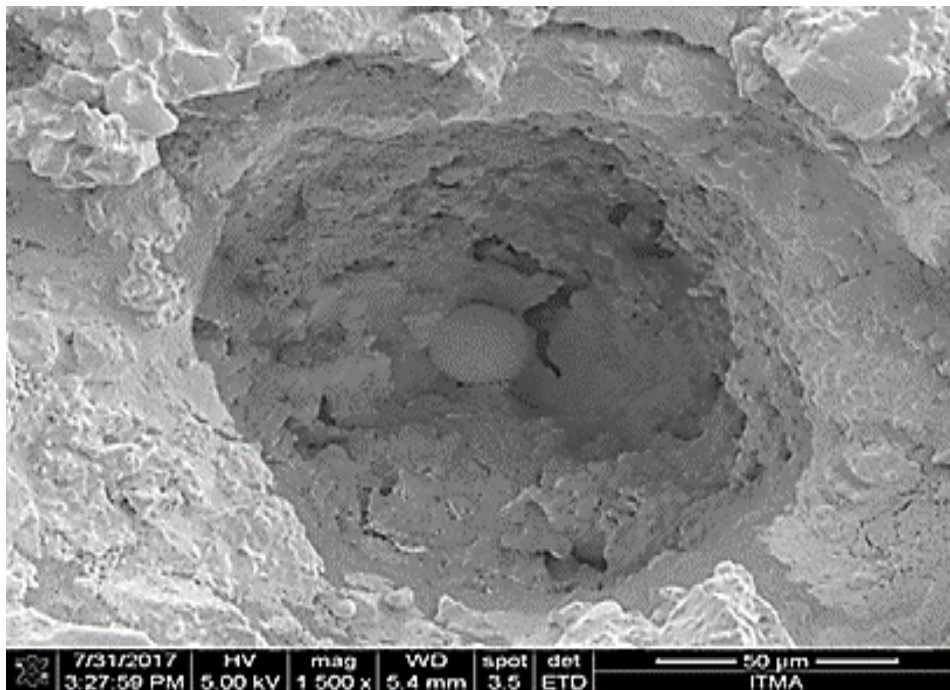


Figure 3: FESEM micrograph for 1 wt. % FCNTs + S (SC-1) subjected to hardness test by micro-Vickers hardness tester

shows a typical FESEM micrograph of a micro Vickers indentation spot in the 1 wt. % FCNTs + S (SC-1) nanocomposite. There are two issues with this method; first, the shape of the impression by the diamond indenter does not reflect its tip, rather, a hollow circular indent was observed which may arise due to the porous nature of the material, consequently, this may question the hardness values to be determined. Secondly, although minor subsidiary cracks can be seen inside the pores, there is a complete absence of classical radial cracks. Therefore,

CONCLUSION

FESEM/EDX, FE-TEM and Raman spectroscopy were used to confirm the survival of CNTs after CNT-silica has been subjected to a high temperature pressureless sintering process at 1450oC for 2 hours dwelling time. Hardness and fracture toughness values by Vickers' indentation could not be obtained due to the porous nature of the surfaces of CNT-silica bricks and lack of classical radial cracks.

Corresponding author: Yusuf T. [ytijani.mec@buk.edu.ng](mailto:ytiijani.mec@buk.edu.ng) Department of Mechanical Engineering, Bayero University, Kano. © 2022. Faculty of Technology Education. ATBU Bauchi. All rights reserved



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