BJET
(Bayero Journal of Engineering and Technology)
https://bjet.ng/index.php/jet

Research Article
2025, Vol. 20 (2), 1-4

TOWARDS HIGH TEMPERATURE APPLICATIONS OF CARBON NANOTUBES CNTS [III]: THERMAL DIFFUSIVITY OF CNTS REINFORCED SILICA NANOCOMPOSITE

Yusuf Tijjani

Department of Mechanical Engineering, Faculty of Engineering, Bayero University, Kano, Kano, Nigeria

Email: ytijjani.mec@buk.edu.ng

Received: 25-06-2025
Revised: 28-06-2025
Accepted: 27-06-2025
Published: 01-08-2025

Abstract: *Consolidated functionalized carbon nanotubes/silica refractory ceramic nanocomposites (FCNTs/silica) were fabricated by pressureless sintering technique. Thermal diffusivity of the nanocomposites with various amounts of carbon nanotubes (CNTs) was investigated. The obtained results demonstrate a modest reduction of thermal diffusivity with temperature; which may suggest that the dominant contribution to the thermal diffusivity is due to the thermally enhanced phonon-phonon scattering. 1 wt. % FCNTs/silica nanocomposite gave the highest thermal diffusivity. Thus, it can be inferred that the CNTs are promising reinforcement for improving thermal diffusivity of the silica refractory ceramics.*

Key words: Silica; Carbon nanotubes; thermal shock resistance; nanocomposites; thermal diffusivity

1 Introduction

Silica refractories are used in the construction of roofs of open-hearth furnace and in the exposed sidewalls owing to their high melting point, rigidity, and strength at elevated temperature (Almarahle, 2005; Alnawafleh, 2009). Low thermal shock resistance; attributed to poor thermal properties; specific heat capacity, thermal diffusivity and thermal conductivity has been identified as the main problem of the silica. Thermal shock resistance depends on/and increase with high values of tensile strength thermal conductivity, thermal diffusivity and fracture toughness; and decrease with low values of coefficient of thermal expansion Young's modulus of elasticity Poisson's ratio and emissivity (Lu & Fleck, 1998).

CNTs possess exceptional thermal properties; for instance, high thermal stabilities up to 2000°C (Kim *et al.,* 2004), and high thermal conductivities (600 W/mK) (Aliev *et al.,* 2010) and thermal diffusivities (D = 39 mm^2/s) (Leahu *et al.,* 2015). Thus, CNTs could be potential reinforcement in a silica matrix to augment its thermal properties. To the best of my knowledge, this is the first research that attempts to determine thermal diffusivity of the FCNTs/crystalline silica refractory ceramic employing also for the first time pressureless sintering technique for consolidation.

2 Experimental Procedure

2.1 Materials

Pristine CNTs (Multiwalled, CVD-grown, > 98 % purity, 10 – 20 nm diameter, and 10 – 30 µm length) were obtained from the Chengdu Organic Chemicals Co., Ltd, Chinese Academy of Sciences, Sichuan Sheng, China. Natural/traditional crystalline silica (as-mined) and clay both were received from quarry site located at Gezawa, Kano, Nigeria. CaO powder (ChemPur®, SYSTERM) was purchased from Classic Chemicals Sdn Bhd., Selangor, Malaysia.

2.2 Determination of particle size distribution of quartzite and clay

The particle size distribution of as-processed silica (as-mined natural crystalline silica subjected to purification, crushing, grinding, and pulverization using crushers, ball mill, and pulverizer) was determined by Mastersizer 2000 E Ver.5.52 (Malvern Instruments Ltd. Malvern, UK), whereas for the clay,

it was soaked in water, dried, and passed through 75 µm metric sieve. The as-passed clay < 75 µm was used for the fabrication of the nanocomposite.

2.3 Acid oxidation of CNTs

The as-received CNT was functionalized by 6M sulphuric acid using ultrasonication at 60°C for 6 h in a procedure similar to what has been described earlier (Buang *et al.,* 2012).

2.4 Preparation of FCNTs suspension

A stable suspension of FCNTs/distilled water was made by ultrasonication using FCNTs/distilled water in the ratio 2:1. The suspension was found to be stable for more than 12 weeks.

2.5 Production of FCNTs/silica nanocomposite

The graded quartzite with average particle size, $d_{(0.5)}$ = 20.166 µm, clay with size < 75 µm and CaO powder were added to portion of the stable suspension of FCNTs as-prepared above. For instance, 5 g of the nanocomposite mixture with 4 wt. % FCNTs (highest percentage of the CNTs used) was made using a wet method by mixing 4.65 g of silica (93 wt. %), 0.20 g FCNTs (4 wt. %), 0.1 g CaO (2 wt. %), and 0.05 g clay (1 wt. %). Thus, obtaining eventually green FCNT/silica nanocomposite test pellets in a similar method as explained by Ahmad *et al.,* 2010. Except for the test specimens here were cold pressed under 90 MPa for 2 min, densified by pressureless sintering technique under argon atmosphere at 1450°C for 2 h with a heating rate of 5°C/min and pellets' dimension; diameter 11 mm x 2 mm height. Also, blank silica pellets were produced in the air under the similar experimental condition for comparison. Then, the as-fabricated/sintered nanocomposites; 0 wt. % FCNTs + S (SC-0), 1 wt. % FCNTs + S (SC-1), and 4 wt. % FCNTs + S (SC-4) were subjected to thermal diffusivity test. Where S stands for silica plus sintering aids (CaO + clay) and C for functionalized carbon nanotubes.

2.6 Determination of thermal diffusivity of densified nanocomposite

Thermal diffusivity values (for the sintered pellets) were obtained by Laser Flash Apparatus LFA 457 Micro Flash (Netzsch, Bayern, Germany). It involves sample preparation and experimental run.

2.6.1 Sample preparation

The sintered pellets (diameter 11 mm x 2 mm height) surfaces were ground and polished to obtain flat and parallel surfaces using emery cloth. Then, the as-ground and polished refractory samples were spray coated on both surfaces with a very thin layer of colloidal graphite. Blackening of the exposed surfaces of the samples maximized the energy absorption.

2.6.2 Experimental run

As demonstrated in Figure 1, the position in the base of the schematic diagram is the head of an Nd: YAG laser. The front side of a disk-shaped flat-parallel sample was illuminated by a short intense expanded laser pulse with a pulse length of 330 µs and a pulse energy output of up to 15 J/pulse. The power was supplied to the laser by a capacitor bank, positioned in a separate box. The power output of the laser has been controlled by the software via the voltage level of the capacitor bank and/or via a filter system positioned in the outlet area of the laser system. The laser pulse was deployed through an enlargement optics system which adjusts the beam diameter to the required sample diameters. From the enlargement optics system, the laser pulse was guided via a mirror through a window into the vacuum-tight sample chamber. Inside the sample chamber is an automatic sample changer for up to three samples carriers which can be adjusted to the actual sample dimensions (square and disk-shaped samples with various diameter, etc.). The resulting temperature rise on the black surface of the sample was measured using either an InSb- or an MCT-infrared detector. Data was acquired via a high-speed amplifier and A/D-converter systems with a maximum possible data acquisition rate of 500 kHz. System control and evaluation of the measurement results were conducted using 32-bits MS ® Windows TM software which allowed fully automatic tests and gave state –of- the art analysis routines for the processed data. The results obtained for the sintered nanocomposite pellets; SC-0, SC-1, and SC-4 are as shown in Table 1.

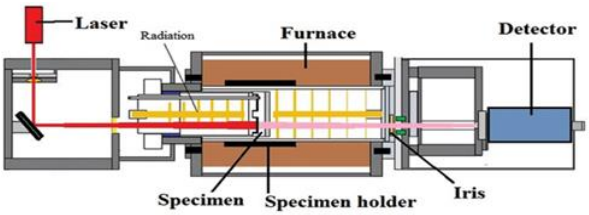

Figure 1: *The schematic of the laser flash method (Yüksel, 2016)*

3 Results and Discussion

3.1 Effect of % FCNTs and temperature on thermal diffusivity of FCNTs/silica bricks

The thermal diffusivity of SC-0, SC-1, and SC-4 at different temperatures are as shown in Table 1 and Figure 2. From the Table and the figure, the thermal diffusivity increases with increased % FCNTs for 1 wt. % FCNTs as compared to that of the unreinforced silica at all experimental temperatures considered. Hence, FCNTs here may be acting as p-type impurity doped into n-type crystalline SiO_2, which improved the thermal properties of the nanocomposite (Wang & Yeow, 2009). The propagation of phonons through the ceramic lattice is largely influenced by the microstructural features such as pores, grain boundaries, and line defects (George *et al.,* 2007). Among these factors, the pores play an important role. The internal walls of bigger pores reflect the incident radiation, conducting heat by radiation with high efficiency. Another factor that can be associated with the value of thermal diffusivity is density. As the density increases, the phonon scattering decreases, thus thermal diffusivity is increased. Consequently, the denser material has less porosity and has more shrinkage. Thus, generally, density and linear shrinkage demonstrate a good trend with thermal diffusivity value. It was reported that other than density and porosity effects, electronics transition effect also contributed to the gain of thermal diffusivity of the sample (Fang *et al.,* 2001). Sample SC-1 has the highest thermal diffusivity for the temperatures considered, even though it has a higher porosity, lower density and lesser linear expansion than the SC-0. Thus, the high thermal diffusivity may definitely come from the contribution of the doped FCNTs; conducting nanotubes disperse randomly in the matrix, connecting opposite faces of the matrix to act as passages for transporting thermal energy (Liu & Fan, 2005). Hence, this should permit a rapid heat flow along the percolated tube network and further improvement of thermal transport (Shenogin *et al.,* 2004a). The increase in diffusivity could be due to the polymorphic phase effect; as there is more amount of tridymite phase in SC-1 than SC-0. The thermal diffusivity decreases as the %FCNTs increases to 4 wt. % for all temperatures. This may be attributed to high porosity and low bulk density of the sample due to the agglomeration of the bundled CNTs which were not infiltrated by the matrix during the sintering process. It may also signify an enhanced phonon scattering, probably due to the covalent interaction between FCNTs and silica. Such interaction would behave like scattering centes for phonons propagating along the tube axis, hence decreasing thermal diffusivity of the nanocomposites (Shenogin *et al.,* 2004b). Furthermore, increasing the nanotubes content may significantly reduce the mean free path of phonons due to the stacking of adjacent nanotubes walls (Liu & Fan, 2005; Yi *et al.,* 1999).

The thermal diffusivities reduce with increased temperature Figure 2. This decreasing trend is obvious; as the temperature increases, the number of phonon collisions increases, their mobility is lower and their capability to transport heat away from the source is less, thus, the thermal diffusivities values decreased. This decrease in thermal diffusivity of the samples with temperature infers that the dominant contribution to the thermal diffusivity could be attributed to thermally enhanced phonon-phonon scattering (Umklapp process) (Liu *et al.,* 1995).

Table 1: Thermal diffusivity of FCNTs/silica @ different temperature

Sample	Thermal Diffusivity, α^2 $(\pm 0.02 \times 10^{-6} m^2 s^2)$ @			
	26°C	300°C	400°C	500°C
SC-0	1.169±0.104	0.582±0.004	0.565±0.007	0.562±0.005
SC-1	1.423±0.036	0.631±0.002	0.617±0.006	0.604±0.007
SC-4	0.497±0.060	0.325±0.003	0.310±0.003	0.305±0.003

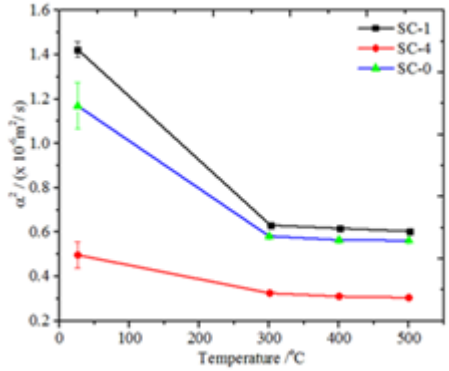

Figure 2: *Thermal diffusivity of FCNTs/silica bricks at different % FCNTs and temperatures*

4 Conclusion

Thermal diffusivity decreases with increased temperature. The diffusivity of SC-1 and SC-4 have been enhanced and reduced respectively for all temperatures considered in the experiments. The

overall findings suggest that the incorporation of functionalized carbon nanotubes (FCNTs) into silica refractory ceramics can improve their thermal properties, importantly: Modest reduction of thermal diffusivity with temperature, with 1 wt. % FCNTs/silica nanocomposite showing the highest thermal diffusivity.

References

Ahmad, I., Cao, H., Chen, H., Zhao, H., Kennedy, A., & Zhu, Y. Q., 2010. Carbon nanotube toughened aluminium oxide nanocomposite. *Journal of the European Ceramic Society*, *30*(4), pp.865-873.

Aliev, A.E., Lima, M.H., Silverman, E.M. and Baughman, R.H., 2010. Thermal conductivity of multi-walled carbon nanotube sheets: radiation losses and quenching of phonon modes. *Nanotechnology*, *21*(035709), p.035709.

Almarahle, G., 2005. Production of silica-refractory bricks from white sand. *American Journal of Applied Sciences, 2* (1), pp.465-468.

Alnawafleh, M. A., 2009. Mechanical and physical properties of silica bricks produced from local materials. *Australian Journal of Basic and Applied Sciences, 3* (2), pp.418-423.

Buang, N. A., Fadil, F., Majid, Z. A., & Shahir, S., 2012. Characteristic of mild acid functionalized multiwalled carbon nanotubes towards high dispersion with low structural defects. *Digest Journal of Nanomaterials and Biostructures*, *7*(1), pp.33-39.

Fang, X., Hing, P., Oh, J.T., Fong, H.S., Chen, X. and Wu, M., 2001. Thermal diffusivity of pure and impurity-doped titanium dioxides ceramics. *Journal of Materials Processing Technology*, *113*(1-3), pp.474-476.

George, S.D., Komban, R., Warrier, K.G.K.,Radhakrishnan, P., Nampoori, V.P.N. and Vallabhan, C.P.G., 2007.
Photoacoustic thermal characterization of porous rare-earth phosphate ceramics. *International journal of thermophysics*, *28*(1), pp.123-132.

Kim, Y.A., Muramatsu, H., Hayashi, T., Endo, M., Terrones, M. and Dresselhaus, M.S., 2004. Thermal stability and structural changes of double-walled carbon nanotubes by heat treatment. *Chemical Physics Letters*, *398*(1-3), pp.87-92.

Leahu, G., Li Voti, R., Larciprete, M.C., Sibilia, C., Bertolotti, M., Nefedov, I. and Anoshkin, I.V., 2015. Thermal characterization of carbon nanotubes by Photothermal techniques. *International Journal of Thermophysics*, *36*(5), pp.1349-1357.

Liu, C.H. and Fan, S.S., 2005. Effects of chemical modifications on the thermal conductivity of carbon nanotube composites. *Applied Physics Letters*, *86*(12), p.123106.

Liu, D.M., Tuan, W.H. and Chiu, C.C., 1995. Thermal diffusivity, heat capacity and thermal conductivity in Al2O3 Ni composite. *Materials Science and Engineering: B*, *31*(3), pp.287-291.

Shenogin, S., Xue, L., Ozisik, R., Keblinski, P. and Cahill, D.G., 2004a. Role of thermal boundary resistance on the heat flow in carbon-nanotube composites. *Journal of applied physics*, *95*(12), pp.8136-8144.

Shenogin, S., Bodapati, A., Xue, L., Ozisik, R. and Keblinski, P., 2004b. Effect of chemical functionalization on thermal transport of carbon nanotube composites. *Applied Physics Letters*, *85*(12), pp.2229-2231.

Wang, Y. and Yeow, J.T., 2009. A review of carbon nanotubes-based gas sensors. *Journal of sensors*, *2009*.

Yi, W., Lu, L., Dian-Lin, Z., Pan, Z.W. and Xie, S.S., 1999. Linear specific heat of carbon nanotubes. *Physical Review B*, *59*(14), p.R9015.

Yüksel, N., 2016. The review of some commonly used methods and techniques to measure the thermal conductivity of insulation materials. In *Insulation materials in context of sustainability*. IntechOpen.