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Microstructural Phase Characterization of Multiwalled Carbon Nanotubes/Quartzite  
Nanocomposite

By

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**ABSTRACT**

*The effects of the addition of multiwalled carbon nanotubes (MWNTs) on microstructural phase properties; peak geometric parameters, crystallite size and residual quartz of sintered MWNTs-quartzite ceramic nanocomposite are determined. MWNTs reinforced quartz ceramic nanocomposite pellets were fabricated by modified conventional powder processing involving pressureless sintering method. The sintered nanocomposite pellets were then prepared and subjected to XRD microstructural technique for comprehensive phase analysis. It has been observed that the crystal properties; peak intensity, FWHM broadening and crystallite size have no effect on the densification property of 1 wt. % MWNTs-quartzite Nano composite. Thus, its thermo-mechanical properties have been influenced by the MWNTs acting as sintering aid mineralizer to convert the residual quartz to tridymite.*

**Key-words:** Quartzite, sintering aid mineralizer, polymorphic silica phases, MWNTS, nanocomposites

**INTRODUCTION**

Natural crystalline silica or quartzite has been traditionally employed as a source material for the fabrication of silica brick. Quartzite, binder; commonly calcium oxide (serving as binder, mineralizer and stabilizer) are the major components used in the preparation of the green molding mixture prior to compaction and firing (Tijjani *et al.*, 2019). The sintering aid mineralizers are those compounds that quicken the allotropic transformation of quartz and cristobalite to tridymite; tridymisation. For instance, iron oxide, barium oxide, magnesium oxide, manganese dioxide, titanium dioxide, nano-TiO<sub>2</sub> etc, have been used in this context (Almarahle, 2005; Brunk, 2000; Manivasakan *et al.*, 2010). Nanocomposites are multiphase solid materials where at least one of the components phases has one dimension less than 100 nanometers (nm) (Ajayan, 2003) Nanocomposite materials have been developed as suitable alternatives to overcome limitations of microcomposites and monolithic materials, while posing fabrication challenges related to the control of elemental composition and stoichiometry in the nano-cluster phase.

In a similar fashion to microcomposites, nanocomposite materials can be grouped based on their matrix materials into ceramic matrix nanocomposite (CMNC), metal matrix nanocomposite (MMNC) and polymer matrix nanocomposite (PMNC). Generally, it is the

reinforcement that is in the nano-range size in these materials (Henrique *et al.*, 2009). Ceramic matrix nanocomposite (CMNC) is based on incorporating nanometer-sized second-phase dispersions into either inter-granular or intra-granular site that is within the matrix grains or on the grain boundaries respectively. Consequently, thermal expansion mismatch between the matrix and second-phase particles produces a remarkable enhancement in physical and mechanical properties such as fracture strength, fracture toughness, creep resistance, thermal shock resistance, and wear resistance (Niihara *et al.*, 1999). For example; it has been reported recently that the addition of multiwalled nanotubes (MWNTs) as second-phase inclusion to the natural crystalline silica/quartzite refractory ceramic matrix had conferred enhancement in physical and mechanical properties; linear/diametric expansion, bulk density, apparent porosity, cold crushing strength, thermal shock cycles, tensile and compressive strengths, Young's modulus, and strain tolerance in tension and compression of the monolithic ceramics (Tijjani *et al.*, 2019; Tijjani *et al.*, 2018).

Thus, the present research would further study the microstructural properties in terms of polymorphic phase transformation of sintered MWNTs-quartzite nanocomposites with a view to establish the implication/function of the MWNTs in the nanocomposites.

## MATERIALS AND METHOD

### Materials

Carbon nanotubes (multiwalled, hydrophilic, 10-20 nm outer diameter OD, 5-10 nm inner diameter ID, 10-20  $\mu\text{m}$  length, > 150  $\text{m}^2/\text{g}$  special surface area SSA, % Purity > 98%, CVD-grown) was supplied by Chengdu Organic Chemicals Co., Ltd, Chinese Academy of Sciences (Sichuan Sheng, China). Quartzite (Gezawa stone) and clay (Gezawa white clay) used for the production of the nanocomposite and plain brick samples were sourced as-mined from Gezawa Local Government Kano State, Nigeria. The CaO powder (ChemPur<sup>®</sup>, SYSTEM); which was used as a binder and mineralizer in the fabrication of the brick samples and sulphuric acid 95-98 % A.R/ACS; for functionalizing/activating the pristine MWNTs were obtained from Ever Gainful Enterprise Sdn Bhd (Subang, Selangor, Malaysia).

### Method

#### Preparation of MWNTS, Quartzite, and Clay

The as-received MWNTs were acid-activated/functionalized using 6M sulphuric acid by ultrasonication as described in the earlier study by Tijjani *et al.* (2019). Similarly, a stable suspension of functionalized MWNTs in distilled water (2:1) was produced by ultrasonication. Both quartzite and clay were soaked in water, dried, ground, and graded to  $d_{(0.5)} = 20 \mu\text{m}$  and < 75  $\mu\text{m}$  respectively.

#### Fabrication of Multiwalled Carbon Nanotube/Quartz Nano composite

As-prepared stable suspension of functionalized MWNTs, powdered quartzite and clay, and CaO powder (mineralizer) were thoroughly mixed, cold compacted, and sintered into sample pellets ( $\varnothing$  21 mm x 8 mm height) via conventional powder processing technique in a similar procedure as explained by Tijjani *et al.* (2018). The produced fired pellets are: Q + 0 wt.% MWNTs (b), Q + 0.01wt.% MWNTs (c), Q + 1 wt.% MWNTs (d), and Q + 4 wt.% MWNTs (e). Where Q is the quartzite + sintering aid (clay +CaO).

## PREPARATION/CHARACTERIZATION OF THE MANUFACTURED NANO COMPOSITES

The samples b, c, d, and e had been ground to powder and subjected to XRD powder analysis.

### *X-ray diffraction (XRD)*

The mineralogical crystalline phases and their nature for the plain as-prepared and sintered powders (a & b) and MWNTs-quartzite nanocomposite powders with a varied amount of MWNTs (c, d & e) were investigated by X-ray diffraction (X'pert Pro Panalytical PW 3040 MPD, Netherlands) using Cu-K $\alpha$  radiation source ( $\lambda = 1.54060 \text{ \AA}$ ) operated at 40 kV and 40 mA. All XRD data were determined under the same experimental conditions of an angular range  $2\theta = 20^\circ - 80^\circ$  using a  $2\theta$  configuration with a step scan of  $0.0330^\circ$  and scan step time of 20 s. For instance, the refractory powdered sample was placed on an aluminium holder. Then, it was positioned in the Goniometer in such a way that the sample surface was horizontally levelled. The sample was illuminated with X-rays of a constant wavelength emanated from copper tube and the intensity of the reflected radiation was recorded. Diffraction patterns were identified using the Joint Committee on Powder Diffraction Standards (JCPDS) powder files. Crystallite size was determined by evaluating the highest intensity of diffraction peak. From the diffraction peak, the width of diffraction at height half way between background and the maximum peak were measured in radian ( $B$ ). Also, by applying Scherrer equation 1.0, crystallite size was calculated.

$$D = 0.94\lambda/B \quad \theta_B \quad 1.0$$

Where,  $D$ ,  $B$ , and  $\theta_B$  are crystallite size, peak FWHM (Full width at half maximum), and peak position respectively. From equation 1.0, crystallite size  $D$  is inversely proportional to peak width  $B$ . This signifies that as peak width gets broader, the crystalline size gets smaller.

## RESULTS AND DISCUSSION

### *Phase Characterization by XRD*

XRD patterns for plain and un-sintered quartzite, plain and sintered quartzite (Q + 0 wt.% MWNTs), and sintered MWNTs-quartzite are shown in Figure 1. The sintering temperature was  $1450^\circ\text{C}$  for 2 hours dwelling time, for all the samples that have been sintered. The plain and un-sintered sample (a) is made of up only one polymorphic phase; quartz (q). This is consistent with the literature as reported by the previous researchers that at room temperature quartzite exist only in the form of quartz (q) (Almarahle, 2005; Chesti, 1986; Manivasakan *et al.*, 2010). As shown in XRD pattern of Figure 1 (b), (c), (d), and (e), they have a similar pattern, peaks position with a comparable set of peaks intensities and appearance of three polymorphic phases; cristobalite, tridymite, and residual quartz. This signifies the successful conversion of the blends upon firing at  $1450^\circ\text{C}$  for 2 hours as reported by Alnawafleh (2009). X-ray powder diffraction was employed to ascertain the extent of this conversion which is essential for deciding the thermo-mechanical properties of silica bricks (Brunk, 2001). As depicted in Figure 1 and Table 1, the sintering process has been able to transform the crystallite size of an un-sintered quartzite brick [sample (a)] from approximately  $0.1\mu\text{m}$  to 72 nm of sintered and plain quartzite brick [sample (b)] (This may suggest some grain refinement during the sintering process). All the crystallite sizes were obtained using Scherrer equation 1.0

Addition of 0.01 and 4 wt. % MWNTs [sample (c) and (e)] to the plain quartzite brick and pressureless sintered under isothermal condition yielded two shorter, maximum peak intensity (as compared to the plain brick (b)) with smaller crystallite sizes 47 nm and 56 nm (Table 1) having the least and second least proportion of tridymite phase (of all the patterns shown in Figure 1) respectively, as obtained from Rietveld analysis. The same argument was partly made; that less tridymite peak intensity may signify lower proportion of tridymite phase (Manivasakan *et al.*, 2010). Considering crystallite as a unit in a grain domain, the reduction or coarsening in crystallite size would definitely amount to reduction or coarsening in grain size. Therefore, the reduction of crystallite size from 72 nm of the conventional quartzite brick to 47 nm and 56 nm for 0.01 and 4 wt. % MWNTs-quartzite nanocomposite bricks could be due to pinning effect by the network of the MWNTs located at the grain boundaries to retard the grain growth and improve densification. Similar behaviour has been mentioned for the CNT/alumina composites; CNTs at the grain boundaries made strong entangled network surrounding the grains to constrains grain growth and enhance density (Inam *et al.*, 2010). In the case of 4 wt. % MWNTs, the pinning effect might have some impediment due to the non-complimentary van der Waals force between the nanotubes as agglomeration set in. Hence, this might be the reasons for further coarsening of the grain size (crystallite size changes from 47 nm to 56 nm, instead of reduction) and deterioration of densification property as the nanotube percentage increase from 0.01 to 4 wt.%. Comparing the Q + 1 wt. % MWNTs [sample (d)] with conventional quartzite brick [sample (b)], they have comparable maximum peak intensity; hence similar FWHM broadening, crystallite size (d; 72.3 nm & b; 72.2 nm) hence, equivalent grain size and density (d; 1.735 g/cm<sup>3</sup> & b; 1.738 g/cm<sup>3</sup>). Thus, it may be assumed that (in this case) the MWNTs have no effect on the densification behaviour of MWNT-quartzite nanocomposites.

This observation is in an agreement with previous study on MWNTs-SiC and MWNTs/alumina nanocomposites (Morisada *et al.*, 2007; Wei *et al.*, 2008). As mentioned earlier, the thermal and mechanical characteristics of quartzite or silica refractory material depend on the most paramount influential parameters in the production of the bricks; these are choice of raw materials and complex transformation behavior of quartzite/silica phases; quartz, tridymite, and cristobalite occurring during sintering or on use. Also, badly transformed silica brick has a considerable critical after-expansion at on-duty temperatures above approximately 1300°C which is the function of the type of quartzite raw material used and residual quartz content. Therefore, as a feature of good conversion, the residual quartz content should be limited to a maximum of 6 % and 1.5 % for coarse-crystalline and crypto-crystalline (or fine crystalline) raw materials respectively (Brunk, 2000; Brunk, 2001). Based on this requirement, only Q + 1 wt. % MWNTs nanocomposite brick with 1.0 % residual quartz (Table 1) can be chosen as candidate brick formulation for better thermo-mechanical properties. The percentage residual quartz has been obtained from Rietveld analysis by X-ray powder diffraction (XRD).

Comparing the selected formulation and the conventional plain quartzite brick, that is sample (d) and (b) and looking for a factor/factors responsible for the conversion of the residual quartz in case of the selected sample to tridymite phase (% tridymite in (d) > % tridymite in (b)). Counting out the sintering temperature and dwelling time (due to the prior trial of 1450 – 1500°C sintering temperature, 2 – 36 hours dwelling and selecting best operating condition based on best specific gravity and low porosity). The next important factor with

respect to conversion is the proportion of mineralizer. In the present research, 2 % CaO as a co-binder and mineralizer (to hasten the polymorphic conversion of quartz to tridymite and cristobalite) is used. The possibility is to further augment the percentage of mineralizer by adding more of CaO or using additional different mineralizers. Manganese dioxide, magnesium oxide, titanium dioxide, etc. have been utilized to speed up conversion of cristobalite to tridymite (Widmann *et al.*, 2001).

Also, It has been reported that addition of 0.25 - 0.5 wt.% nano-titania to the conventional silica brick reduces the residual quartz content, hence increases the tridymite phase content, and consequently resulted in a brick with better refractory properties (Manivasakan *et al.*, 2010). Similarly, in the present research, for the first time, we are reporting another novel application of MWNTs (precisely 1 wt. % MWNTs) as a sintering aid mineralizer; that would reduce the proportion of residual quartz content via its conversion to tridymite phase for enhancing the physical refractory properties of quartzite brick. Consistent with our finding, it has been insisted that the CNTs should not only be regarded as an additive for enhancing the properties of ceramics due to their excellent intrinsic physical properties but also should be considered as a sintering aid to control sintering characteristics and microstructures (Inam *et al.*, 2010; Milsom *et al.*, 2012; Zahedi *et al.*, 2015). Also, our findings could be responsible for the reported high thermal shock cycle in 1 wt.% CNTs/silica nanocomposite (Tijjani *et al.*, 2019).

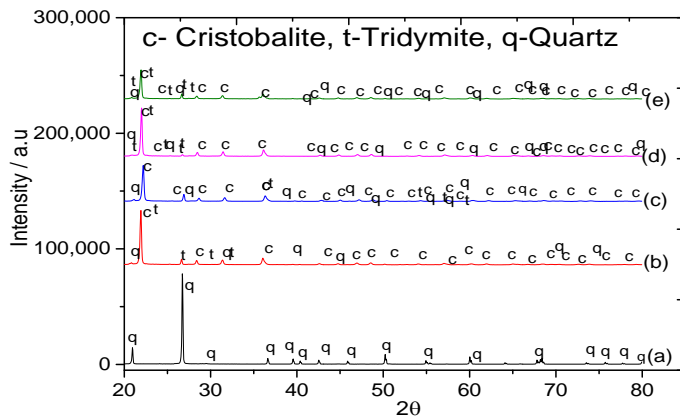


Figure 1: XRD pattern of (a) plain & un-sintered quartzite, sintered : (b) Q + 0 wt.% MWNTs (c) Q + 0.01 wt.% MWNTs (d) Q + 1 wt. % MWNTs (e) Q + 4 wt. % MWNTs

Table 1: Peak geometric parameters, crystallite size and residual quartz

Sample	a	b	c	d	e
%FMWNTs	-	-	0.01	1	4
Maximum peak intensity/quartz (%)	100	-	-	-	-
Maximum peak intensity/(cristobalite/tridymite) (%)	-	100/100	100/14.98	100/100	100/100
FWHM/quartz (2θ)	0.1299	-	-	-	-
FWHM/(cristobalite/tridymite) (2θ)	-	0.1624	0.2273	0.1624	0.1948

Sample	a	b	c	d	e
Position/quartz (2 $\theta$ )	26.7238	-	-	-	-
Position/(crystalite/tridymite) (2 $\theta$ )		21.9102	22.1905/ 36.2796	21.9862	21.9277
Crystallite size [Å]	1021	722	457/472	723	558
Crystallite size [μm]	0.1021	0.0722 (72.2 nm)	0.0457/0.0472 (45.7/47.2 nm)	0.0723 (72.3 nm)	0.0558 (55.8 nm)
Residual quartz [%]	-	8.0	14.0	1.0	11.0

## CONCLUSION

It has been determined for 1 wt. % MWNTs-quartzite nanocomposite; possess the least amount of residual quartz; thus high amount of tridymite, and an enhancement in thermo-mechanical properties. Hence, there is possibility of MWNTs acting as mineralizers in a conventional green silica refractory brick/ramming mixtures.

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