

## Mechanical properties of *in-situ* growth carbon nanotubes reinforced porous ceramics by direct foaming

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This paper reports the formation of carbon nanotubes (CNTs) reinforced porous Al<sub>2</sub>O<sub>3</sub> ceramics by a novel combination of three processes. Porous ceramics are developed using direct foaming. Cobalt nanoparticles as catalysis agents are simultaneously synthesized and dispersed by colloidal process to prepare the suitable catalyst material for carbon nanotubes synthesis. The catalytic chemical vapour deposition (CCVD) technique is used to directly synthesize CNTs within the porous ceramics and the effect of growth time on the morphology, crystallinity and yield of CNTs are investigated. Hertzian indentations are used to evaluate the damage behaviour under constrained loading conditions. The mechanical behaviour from indentation load-displacement curves is compared according to CNTs contents in the samples.

**Key words:** Carbon nanotubes, Porous ceramics, Colloidal process, Hertzian method, Quasi-plastic behaviour.

### Introduction

Porous ceramics having high stiffness and thermal stability and relatively low density are considered good constituents for the fabrication of advanced composites requiring high chemical and thermal stability [1, 2]. The combination of CNTs and porous ceramics to develop functional composites offers a very attractive system that contributes to research and development.

In recent years, carbon nanotubes reinforced ceramic foams like Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and SiC have been reported, and these foam ceramics possess high-temperature stability, as well as enhanced mechanical properties [3, 4]. However, the aggregation of CNTs in ceramic matrix, and random bonding between matrix and reinforcement present major problems [5, 6]. Thus, it is necessary to develop novel approaches to obtain *in-situ* growth carbon nanotubes reinforcement of porous ceramics and to create composite foam of suitable mechanical behaviour. Due to their low density, and excellent mechanical and thermal properties, CNTs have been the subject of intensive research as an ideal reinforcement for ceramic composites, to both the strength and lower the weight of composites [7, 8].

To obtain a homogeneous distribution of CNTs in ceramic matrix and a good interface between the CNTs and porous matrix, a novel approach towards the

reinforcement of CNTs grown in porous ceramics was attempted, by the harmonization of three different reaction techniques. Producing a fine dispersion of catalyst particles contributes significantly to their stabilization. This helps in preserving their morphology at CVD processing temperatures, which results in increased nucleation sites, leading to high-yield CNTs production [9, 10].

This study reports three different techniques for CNTs reinforced porous ceramics; firstly, porous ceramics were synthesized by a direct foaming method using Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> as starting materials. Secondly, Co nano-particles were synthesized and dispersed homogeneously within the wet foam by colloidal processing. Finally, *in situ* growths of CNTs were investigated by CCVD, in which catalytic nanoparticles, placed in the porous ceramics, were used as catalyst for the reinforcement of CNTs.

### Experimental

#### Suspension preparation for wet foam

Fig. 1 shows schematics of the synthesis of CNTs within porous ceramics. Al<sub>2</sub>O<sub>3</sub> powder (d<sub>50</sub> ~ 4 mm; KC, South Korea), and SiO<sub>2</sub> powder (d<sub>50</sub> ~ 3.5 mm, Junsei Chemicals Co. Ltd., Japan) were added to de-ionized water, and the aqueous suspension was prepared separately. Homogenization and de-agglomeration of the suspension was carried out using polyethylene bottles on a ball mill for at least 48 hrs at a rotation speed of 60 rpm, and zirconia balls (10 mm in diameter), with ball/powder ratio 2 : 1. After ball milling, propyl gallate (Fluka Analytical, Germany) as a surface modifier at

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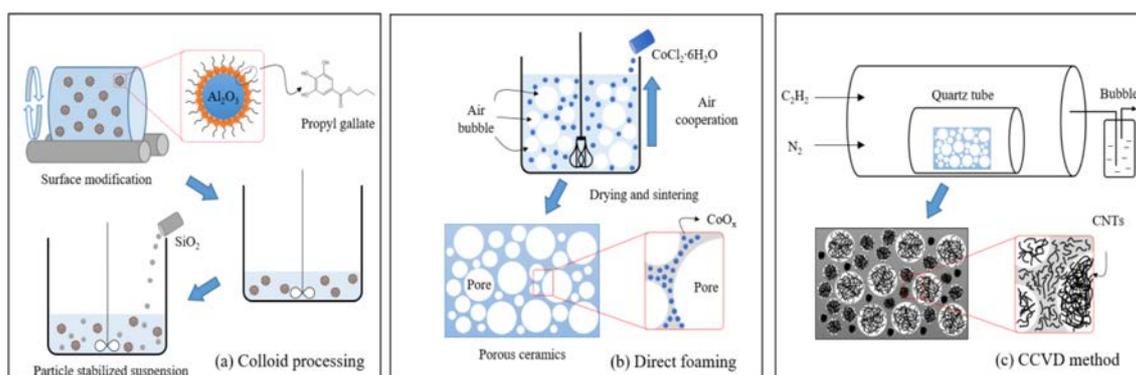


Fig. 1. Schematic diagrams of the synthesis of CNTs within porous ceramics.

0.2 wt% amount was added to the  $\text{Al}_2\text{O}_3$  suspension under mechanical stirring, to hydrophobize the surface of  $\text{Al}_2\text{O}_3$  particles. The pH of the suspension was adjusted to 4.75, by adding drop-wise (4) M NaOH and/or (10) N HCl (Yakuri Pure Chemicals, Japan). The solid content of the final aqueous suspension was set to 30 vol%, by adding the required amount of water. Then, the  $\text{SiO}_2$  suspension, which was also homogenized and ball-milled, was then added to the  $\text{Al}_2\text{O}_3$  suspension in molar (1 : 0.25) concentration [11]. Foaming of the resultant mixture was carried out using a hand mixer (150 watt, Super Mix, France) for 15 minutes. The wet foams were dried and sintered at 1300 °C for 1 hr to obtain the porous ceramic matrices.

### Preparation of the Co-catalysis and CNTs reinforced porous ceramics

First, a certain amount of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.12 mol%) was dissolved in 250 mL of deionized water by magnetic stirring. Then, this solution of 10ml was mixed stepwise to  $\text{Al}_2\text{O}_3/\text{SiO}_2$  final suspension with vigorous stirring under ambient condition, to disperse nanoparticles in wet foam. Secondly, the wet foam was dried at ambient temperature and calcined at 723 K under nitrogen ( $\text{N}_2$ ) flow for 3 hrs prior to the CNT synthesis. The Co-containing  $\text{Al}_2\text{O}_3$  porous ceramics were designated as CoA/C. Catalytic decomposition of acetylene on the CoA/C sample was carried out in a quartz boat centered in a horizontal tube furnace. Finally, the temperature was raised at a rate of 5 °C/min to the desired reaction temperature in nitrogen atmosphere (500 sccm). Carbon nanotubes were grown by the introduction of carbon feeding gas  $\text{C}_2\text{H}_2$  (10 sccm) at 650 °C. CNTs were separately synthesized for 60, 120 and 180 min and the four samples were termed CNT1, CNT2, and CNT3, respectively.

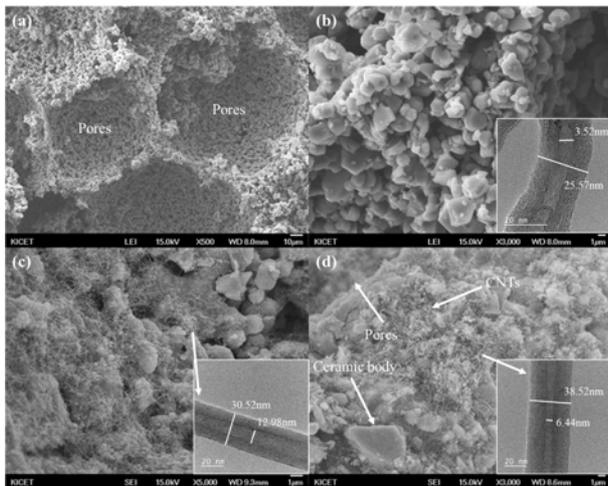
### Materials properties

The microstructures of CNTs-reinforced porous ceramics were observed by field emission scanning electron microscopy (FESEM) (Jeol, Japan) and high-resolution transmission electron microscopy (HRTEM)

images were taken on a Jeol JEM-3011 at an accelerating voltage of 200kV. Thermogravimetric analysis (TGA) of the dried samples was carried out using a thermal analyser (Shimadzu, Japan) in static air up to 1400 °C at a heating rate of 10 °C/min. The analyses of CNTs materials were characterized by Raman Spectroscopy with a system FRA-106/S, using a laser excitation line at 1064 nm (Nd-YAG). The mechanical behaviour of the load-displacements curves of the sintered CNTs reinforced porous ceramics was investigated using Hertzian indentations tests. Cylindrical specimens of 1 inch in diameter were cut from the as-received materials and polished. Hertzian indentation tests were performed on the polished surface in air with a universal testing machine (Model 5567, Instron Corp., Canton, MA) at a constant cross-head speed of 0.2 mm/min over a load range of  $P = 5 - 200$  N, using tungsten carbide spheres of radius  $r = 7.93$  mm. The load-displacement curves were plotted during loadings. After measuring by extensometer, the displacements were consecutively converted through amplifier, converters, and a digital signal processor.

### Results and Discussions

Fig. 2(a) shows a FESEM and corresponding TEM images in the inset of the porous ceramics obtained by direct foaming that was used as the substrate for CNTs synthesis. The microstructure of the ceramic body obtained, shows a great number of open, interconnected pores leading to a high porosity of up to 80%. The interconnected pores ensure the penetration of carbon feedstock through the porous ceramics resulting in a composite with CNTs spreading inside and interfacing the porous ceramics. Figs. 2(b-d) show FESEM images of the CNTs synthesized by CCVD technique on the porous ceramics for 60, 120 and 180 min, respectively. While the insets of the images show a much larger area of the porous ceramics after CCVD, parts of them are magnified to show the CNTs synthesized on them. A dense population of CNTs synthesized randomly all over the porous ceramics is clearly evident in all the images. Fig. 2(b) shows that the length of CNTs produced in the

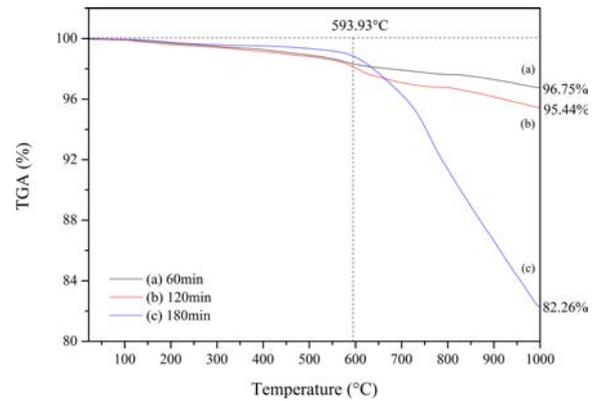


**Fig. 2.** FESEM and HRTEM micrographs of (a) porous ceramics by direct foaming synthesized CNTs at 650 °C for (b) 60, (c) 120, and (d) 180 min/

inset for 60 min (CNT2) is comparatively shorter and not fully-grown. Fig. 2(c) shows that CNT3 exhibits longer CNTs grown in the inset an entangling fashion creating a close network. As described by this work, a growth time of 60 min or more, can be considered appropriate for normal CNTs synthesis and for enhancement of mechanical properties as shown in Fig. 5.

Fig. 2(c) shows that CNT3 in the inset has outer walls of 30.52 nm with better smoothness. Also, note the apparent growth of the inner and outer diameters of the nanotubes. It can be inferred that the decomposition of carbon atoms from  $C_2H_2$ , forming coaxial cylindrical graphene sheets layer by layer around the CNT core, is strongly related to the reaction time [7]. Figs. 2(b-d) in the inset shows that the thickness, crystallinity and yield of CNTs also display a growth tendency with the increase of reaction time as shown in Table 1. All of the CNTs samples possess bamboo-like structures and are typically multi-walled CNTs (MWCNTs).

Fig. 3 shows TGA curves for the synthesized CNTs. All of the samples exhibit an initial weight loss tendency, which may be attributed to the loss of physically adsorbed water by the zeolites [7-9]. In the subsequent heating process, all of the four CNTs samples underwent a similar weight loss tendency with heating, presenting a single-step weight loss pattern. Usually, the decomposition of  $C_2H_2$  on metal catalysts leads to the formation of CNTs as well as amorphous carbon particles, which can be identified in TG curves as a two-step weight loss process [10]. Therefore, the single-step weight loss pattern exhibited here indicates the absence of other carbonaceous products and the sole presence of CNTs exhibiting good crystallinity and high purity. This result is in accordance with the TEM images. The quantity of carbon deposited during the decomposition of hydrocarbon molecules on metal-containing catalysts by CVD is usually calculated as follows:

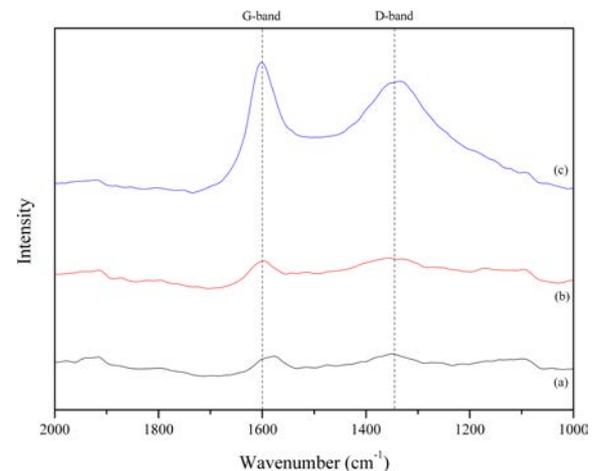


**Fig. 3.** TGA curves of CNTs synthesized at 650 °C for (a) 60, (b) 120, and (c) 180 min.

$$\text{Carbon yield (\%)} = \frac{(m_{\text{tot}} - m_{\text{cat}})}{m_{\text{cat}}} \times 100\% \quad (1)$$

where,  $m_{\text{cat}}$  is the initial catalyst amount (before the reaction) and  $m_{\text{tot}}$  is the total sample weight after the reaction. The use of TGA data allows the determination of the amount of deposited carbon. Table 1 shows the estimated amount of carbon yield % for all the produced ceramics-zeolite-CNT composites.

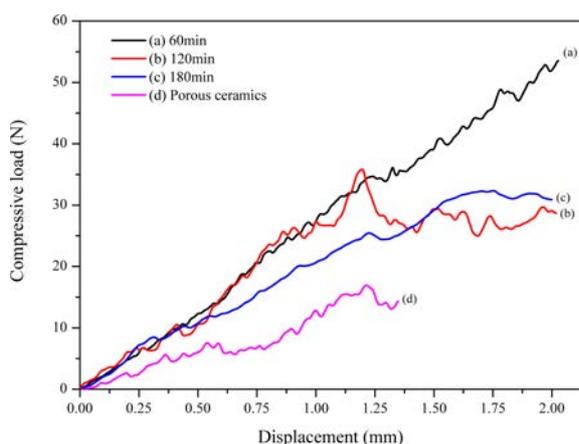
Fig. 4 shows the Raman spectra for the CNTs synthesized for 60, 120 and 180 min. Two strong peaks of around 1339 and 1600  $\text{cm}^{-1}$  dominate all three spectra. The accepted nomenclatures for these two peaks are D- and G- bands, respectively. They are characteristic of disordered  $sp^2$ -hybridised carbon materials and have been



**Fig. 4.** Raman spectra of CNTs synthesized at 650 °C for (a) 60, (b) 120, and (c) 180 min.

**Table 1.** Quality of CNTs (Raman spectra) and carbon yield % (TGA) with respect to reaction temperature.

Sample name	Reaction time [min]	Raman ratio [ $I_D/I_G$ ]	Carbon yield [%]
CNT1	60	1.00	1.58
CNT2	120	1.00	2.71
CNT3	180	0.99	16.59



**Fig. 5.** Hertzian indentation load-displacement curves of CNTs synthesized for (a) 60, (b) 120, and (c) 180 min using WC sphere with a radius of  $r = 7.93$  mm. The comparative curve of (d) porous  $\text{Al}_2\text{O}_3$  ceramics was inserted in the graph.

observed in all reported Raman spectra of MWCNTs [12]. The D-band is formed by defects in the graphite crystals, and by the finite sizes of graphite crystallites in the material. Moreover, pyrolytic carbon particles deposited on the nanotubes also contribute to the rise of D- band. The G- band corresponds to the tangential stretching ( $E_{2g}$ ) mode of highly oriented pyrolytic graphite (HOPG) and indicates the presence of crystalline graphitic carbons in the MWCNTs. The strength of the D-band relative to the G- band is a measure of the amount of disorder in the CNTs, and is used for qualitative characterizations of the nanotubes. Table 1 also provides the relative intensities of the D- to G- bands ( $I_D/I_G$  ratio), as revealed by the Raman spectroscopy, which is a measure of the degree of graphitization. The  $I_D/I_G$  values from this work are between 0.99 and 1.00, which accord with that reported in the literature ( $I_D/I_G = 0.7-1.3$ ) for CVD-grown MWNTs [13], revealing the high quality of CNTs grown in this experiment.

Fig. 5 shows Hertzian indentation load-displacement curves for CNTs-reinforced porous  $\text{Al}_2\text{O}_3$  ceramics synthesized sintered at  $650^\circ\text{C}$  for 60, 120, and 180 min. which plot indentation load  $P$  against displacement  $\delta$ . The indentations were performed using WC sphere with a radius of  $r = 7.93$  mm. As the growth time is not enough for CNT1, we indented the samples of CNT2, and CNT3 with a comparative porous  $\text{Al}_2\text{O}_3$  sample without CNTs. Note that the curve for porous ceramics is considerably lower and flatter than that for CNTs reinforced porous ceramics, indicating a much softer, so quasi-ductile material. However, this behaviour indicates a “high damage tolerance” of the specimens under constrained spherical indentation. It is worthwhile noting that the indentation load is almost constant over the entire displacement range of sample porous ceramics. Whereas, the cases of the sample with CNTs content, by reaction for 60 min for example, show an increasing load with displacement, indicating a much higher loading

support with smaller displacement. On the other hand, the quasi-ductile properties by carbon nanotube become more dominant with increasing amount of CNTs, which corresponds to our prior results indicating the dependence of damage and wear resistance of  $\text{Al}_2\text{O}_3$ -CNT composites on the CNT content [14].

## Conclusions

CNT-porous alumina ceramic composite containing an extensive quantity of MWCNTs within, were formed by a novel processing route that unified three independent processing techniques in, succession. Owing to the high porosity of porous ceramics matrix, acetylene supply to the catalytic metal nanoparticles was very easy, leading to the growth of uniform and dense CNTs across the entire porous alumina ceramics. A range of time (40, 60, 120 and 180) min were investigated and 180 min was chosen as the optimum time which led to the highest yield of CNTs of about 16.59%. The results indicated distinctive differences in morphology, yield content, and crystallinity with different reaction temperatures. The microstructures obtained in  $650^\circ\text{C}$  temperature exhibited considerable wall thickness, and the widest inner hollow tube structure. Raman spectroscopy, which is a measure of the degree of graphitization, revealed the relative intensities of the D- to G- bands ( $I_D/I_G$  ratio) were between 0.99-1.00, which are within the range of values reported in the literature ( $I_D/I_G = 0.7-1.3$ ) for CVD grown MWCNTs. The addition of CNT could enhance the elastic modulus of porous  $\text{Al}_2\text{O}_3$ . The quasi-ductile property of the composite was found at more than 10% CNTs.

## Acknowledgements

This work was financially supported by Hanseo University, Korea.

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