

Silicon nitride/ carbon nanotube composites: preparation and characterization

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Abstract. This paper investigated the preparation of silicon nitride composites with multiwalled carbon nanotubes (MWCNTs). Samples containing 1–10 wt% MWCNTs were ultrasonically processed in non-aqueous suspensions, dried, pressed, and then subjected to pressureless sintering at 1600 °C for 2 h. The preliminary results showed that the mixture of activated silicon nitride and covered MWCNTs could be sintered. The porosity of the obtained samples ranged from 0.27–36.94 vol.%. The microstructure was observed by scanning electron microscopy (SEM), and the mechanical properties (hardness and fracture toughness) were also determined. Good hardness values were obtained for samples prepared by sintering the mechanically-activated precursor under flowing nitrogen atmosphere using the lowest fraction of CNTs. Residual activator reduced the densification of the composites.

Key words: mechanochemical activation; sialon; mechanical properties; silicon nitride; carbon nanotubes

1. INTRODUCTION

Carbon nanotubes (CNTs) are derivatives of fullerenes that are terminated with fullerene hemispheres. The diameters of the smallest nanotubes are approx. 1 nm. Since the length-to-diameter ratio (L/D) of a nanotube can be approx. 10^2 – 10^3 , nanotubes can be treated as one-dimensional materials. By inserting nanotubes with different diameters inside one another, multiwalled nanotubes can be obtained [1].

Nanotubes have several interesting properties [2-3]:

- Very strong bonds between carbon atoms give the nanotubes extreme durability.
- Nanotubes have a high Young's modulus (approx. 10^{12} N/m²). Due to this, they can undergo elastic deformation and are resistant to ultimate tensile and bending.
- Nanotubes can conduct high-density electrical currents (approx. 10^9 A/cm²), compared with 10^3 A/cm² for copper.
- Nanotubes have very high specific thermal conductivity, reaching 6000 W/(m·K) (copper approx. 400 W/m·K) at $T = 300$ K, which can be useful for heat removal from electronic elements, where overheating is still a serious problem.

In connection with the above, and thanks to a combination of several useful properties of carbon nanotubes, they can be doped into ceramics to produce composites with considerably increased electrical conductance and/or thermal conductivity. Additionally, improvements in the mechanical properties, such as fracture toughness or flexural strength, can be expected;

however, these properties of ceramics depend, to a high degree, on the microstructure of composites with a ceramic matrix and the presence of critical slots, where the number and size are controlled by the technological conditions (homogeneity of samples and sintering conditions) and the presence of anisotropic inclusions (i.e., nanotubes), which do not provide favorable conditions to improve the homogeneity of molded pieces; thus, the mobility of grain boundaries is lower during sintering. One can expect that obtaining low-porosity ceramic/carbon nanotube composites will be a great technological challenge, as shown by preliminary results [4-6]. A ceramic matrix must be chosen to obtain attractive carbon nanotubes composite should consider stability in a ceramics – carbon join in sintering conditions, which eliminates a majority of oxide ceramics. Silicon nitride is one such candidate because it is stable in the presence of carbon up to 1500 °C, and above this temperature, it can form silicon carbide. Ceramics derived from silicon nitride have excellent mechanical properties at low and high temperatures, but nitride ceramics are often not as porous and are deprived of oxygen, preventing them from achieving high thermal conductivities (120 W/mK at 300 K), and expensive final treatment of ready elements remain basic problems. Thus, obtaining electro-conductive ceramics using a Si₃N₄ matrix is an attractive technical task of an innovative nature on a global scale because previous attempts to obtain Si₃N₄-CNT composites have been met with limited success.

This is primarily because of the inhomogeneous distributions of fibers in the matrix and the porosity of sinters, despite extreme sintering conditions (e.g., iso-static sintering under pressure (HIP) at 1700 °C and a pressure of 20 MPa [7-10]) and/or a decline in fibers during sintering. The most recent results [10] have revealed that it is possible to obtain electrically-conductive composites after introducing 5% weight CNTs and using low isostatic sintering pressure (HIP – high pressure, 2 MPa at 1700 °C); however, the homogenization of mixtures required both ultrasound impact and common milling of a ceramic precursor and nanotubes.

Increasing the sinterability of ceramics based on silicon nitrides can be achieved using mechanochemical activation of a precursor, which has been used to sinter sialon ceramics [11-17]. As a consequence, the concentration of CNTs in composites should be less extreme.

In this paper, an innovative attempt to form Si₃N₄-CNT composites was undertaken by applying mechanochemically-activated ceramic powder and carbon nanotubes. The purpose of this paper was to obtain preliminary results that define the sintering ability of a mixture of activated silicon nitride with sintering additives and nanotubes.

2. MATERIALS AND METHODS

The silicon α -nitride powder (Sigma Aldrich), aluminum nitride (H.C. Starck), and yttrium oxide sintering additive (H.C. Starck) were used to obtain a nitride matrix. The initial mixture is specified in Table 1.

TABLE 1. Composition of the precursor and properties of initial powders.

Component of mixture	Weight fraction %	D50, [μm]	BET, [m ² /g]	Density, [g/cm ³]
α -Si ₃ N ₄	89.3	1.30	1.58	3.19
AlN	5.7	2.41	0.47	3.26
Y ₂ O ₃	5.0	0.90	10.0	5.01

The milled sample powders were characterized by specific surface area measurements (BET). Carbon nanotubes were added after mixing and activated using grinding. A product obtained from the International Institute of Metallurgy in Dnepropetrovsk (Ukraine), by a method of CO catalytic distribution in the presence of concentrated sulfuric acid and formic acid, was the source of MWCNTs. The synthesis was performed in a tube furnace under atmospheric pressure. Metallic catalyst (20–50 mg) in the form of Fe was refined to nanoparticle sizes and then placed in a quartz tube. Amorphous carbon, collected on the catalyst surface, particles of metal, surrounded by graphene layers, and multiwalled nanotubes were the products of catalytic pyrolysis. Before being added to tested mixtures, nanotubes underwent ultrasonication, as in the case of the Y₂O₃ substance. Four mixtures were prepared, and 1 g carbon nanotubes were added to two of them, and 0.1 g carbon nanotubes were added to the other two. Having added the nanotubes, de-agglomeration was carried out using ultrasonication.

Two mixtures are specified in Table 2.

TABLE 2. Characteristics of the prepared mixtures.

Number of mixture	Components [g]	Milling bodies	Mixing (roll bench)	Milling (planetary mill)
N	100	Si ₃ N ₄	propanol/24 h evaporation/ 110°C/24	-
TTD (de-agglomeration1)	100	Si ₃ N ₄	propanol/24 h	acceleration 28g/30min

1- 66% dissolvent and MEK (methyl ethyl)/34% ethyl alcohol were prepared, - in small volume of dissolvent, 3% weight of surface active agent KD1 (3% in relation to solid parts (powder)) was dissolved, - 5% weight Y₂O₃ was added do dissolvent with KD1 and it underwent action of ultra-sounds for 1 hour time duration, power of a device was 70% max power, max temperature was 85°C, - remained powder was added to the Y₂O₃ de-agglomerated substance and then dissolvent, in suitable volume, was added in order to get good liquefaction,
- the whole of mixture underwent impact of ultra-sounds in the same conditions as previously.

After drying in a chamber drier at 110 °C for 24 h, 3 g samples (\emptyset : 20 mm, h : 5–6 mm) were formed. These samples were pressed on a hydraulic press (uniaxial pressing) under a pressure of 250 MPa. The reaction sintering procedure was identical for both kinds of specimens. The pressed tablets were contained within a powder bed of Si₃N₄/BN within a BN crucible with a lid. Sintering was carried out in a graphite furnace (Thermal Technology) under flowing nitrogen at 1600 °C for 2 h. The size and mass of the specimens were controlled. The density was determined by Archimedes' method in distilled water. Vickers's hardness tests and the fracture toughness K_{Ic} were measured on a Zwick Material Testing 3212002/00 hardness testing machine under a pressure of 100 N. Hardness tests were carried out on polished samples at room temperature with a diamond indenter. The critical coefficient of the K_{Ic} stress intensity was determined on a ground by analyzing the ratio of the diagonal length of the impression to the crack length. These cracks were obtained as a result of the Vickers's hardness tests. From the analyses, in each hardness test, Palmqvist-type cracks occurred, which was proven by determining the ratio of the crack length to the diagonal of the impressions. Microstructure tests were carried on mounted and polished samples using a HITACHI S-3400N scanning electron microscope, equipped with auxiliary devices (EDS, Thermo NORAN+ system SIX). XRD measurement were performed in the 10-90° 2 θ range with Cu K α radiation and an incident beam monochromator (X'pert, Philips-Panalytical).

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3. RESULTS AND DISCUSSION

In the case of applying a planetary mill, a considerable increase in the surface area ($16.8 \text{ [m}^2/\text{g]})$ was observed compared with the initial mixture, which did not undergo grinding and was only mixed on a rolling bench ($5.2 \text{ [m}^2/\text{g]})$.

Microscope observations of carbon nanotubes showed that their thickness was considerable, approx. 100 nm. The presence of iron was proved by EDS, so we suspect that they were contaminated with residual Fe catalyst.

Sintering of the composites revealed the basic influence of the presence and quantity of CNTs on their susceptibility to sintering. The obtained results (Table 3) show that the lowest porosity of composites was obtained in the case of the sample without carbon nanotubes, which was activated in a planetary mill at high acceleration (TTD) and in the case of the TTD samples with 1% carbon nanotubes. In these cases, the highest apparent density (approx. 3 g/cm^3), comparable with the results in ref. [10], was obtained when sintering under isostatic pressure (HIP). The worst results were noticed in the case of samples with 10% nanotubes prepared by mixing on a roll bench and samples that were milled at high acceleration. It was noticed that 1% weight CNT addition to the precursor only slightly lowered its susceptibility to concentration comparing with a sample without nanotubes, regardless if the precursor was activated or not. The activated precursor sintered itself almost entirely (porosity: 0.27 vol%). On the other hand, the introduction of 10% CNTs changed the microstructure of the composite, and the activation of the precursor only slightly improved the sinterability. The obtained results indicate the decisive role of mechanochemical activation of the precursor on the concentration of these composites unless the number of introduced nanotubes is below a certain critical value. The applied dispersion methods appeared to be insufficient.

The hardness test results showed that samples ground in a high-energy planetary mill with an acceleration of 28 g for 30 min had the highest hardness (TTD, 13.76 [GPa]). Comparable results were obtained for samples with low additions of carbon nanotubes, sample 1 TTD (12.48 [GPa]). In other cases, it was impossible to test samples under the given charge of 100 N because of their considerable porosity. Fracture toughness determined using Evans's method from the Palmqvist's crack length measurements did not provide reliable results.

The microstructure showing the lateral fracture of the obtained sinters are presented in Figs. 1–4. In all tested cases, clusters of fibers with considerably larger (10 times) diameters compared with the coated nanotubes were obtained.

TABLE 3. Results of the measurements of open porosity, apparent density, and relative density, determined by Archimedes' method of samples sintered at 1600°C for 2 h.

Participation of nanotubes Wt %	Time of mixing/grinding	Density of tablets $[\text{g/cm}^3]$	P_o^1 [%]	ρ^2 d_v $[\text{g/cm}^3]$	ρ^3 [%]
N	24h	1.68	26.25	2.36	40.18
1N	24h	1.67	26.22	2.28	37.08
10N	24h	1.48	36.94	1.99	34.03
TTD	30 min	1.88	0.27	3.14	67.23

1TTD	30 min	1.88	5.78	2.90	54.34
10TTD	30 min	1.63	32.00	2.12	30.26
¹ open porosity after sintering process					
² apparent density after sintering process					
³ relative density after forming					

The presence of light spherical inclusions on the ends of fibers (Figure 2) reveals an increase in the number of these fibers by the vapor-liquid-crystal (VLS) method, where an iron silicide (Fe_nSi) alloy was formed as a result of the reaction between Fe and $\text{SiO}_{(g)}$, the latter of which was formed in the presence of carbon (CNT).

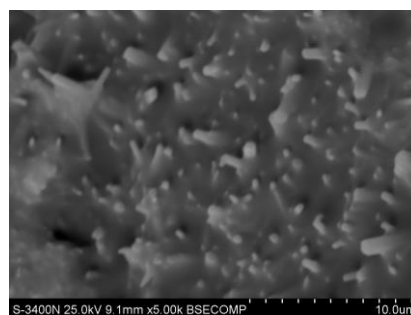


Fig.1. The microstructure of a fracture in a doped sample containing 1% coated carbon nanotubes. Samples were prepared from an activated precursor in a high-energy planetary mill and sintered at 1600°C for 2 h (1 TTD).

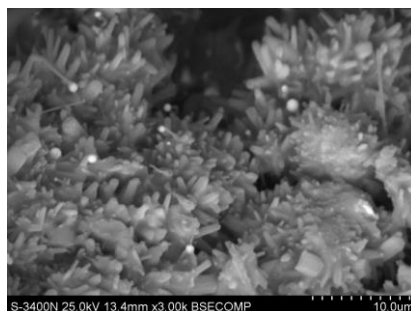


Fig.2. The microstructure of a fracture of a doped sample containing 10% coated carbon nanotubes. Samples were prepared from an activated precursor in a high-energy planetary mill and sintered at 1600°C for 2 h (10 TTD).

This mechanism occurred in all composites with a considerable number of CNTs (Figure 3 and Figure 4) and may be responsible for the low concentration of these materials. The observed fibers may be Si_3N_4 fibers, maybe increasing ones on primary carbon nanotubes. The microstructure of the fracture of the composites doped with 1% CNT using an activated precursor appears slightly different: the low porosity was due to the considerable susceptibility to concentration. The same unfavorable phenomenon of mass transfer by evaporation and condensation was limited, and the observed fibers may be the initial nanotubes (Figure 1).

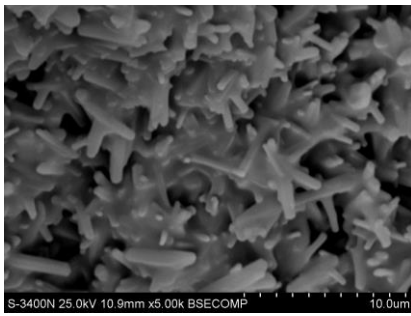


Fig.3. The microstructure of a fracture in a doped sample with 1% coated carbon nanotubes. Samples were prepared by mixing on a roll agitator and sintering at 1600°C for 2 h (1 N).

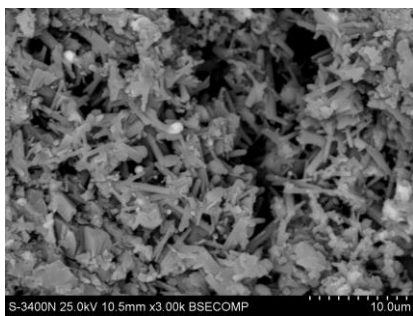


Fig.4. The microstructure of a fracture in a doped sample with 10% coated carbon nanotubes. Samples were prepared by mixing on a roll agitator and sintering at 1600°C for 2 h (10 N).

The phase composition of the mixtures after sintering, as detected by XRD, is given in Fig. 5.

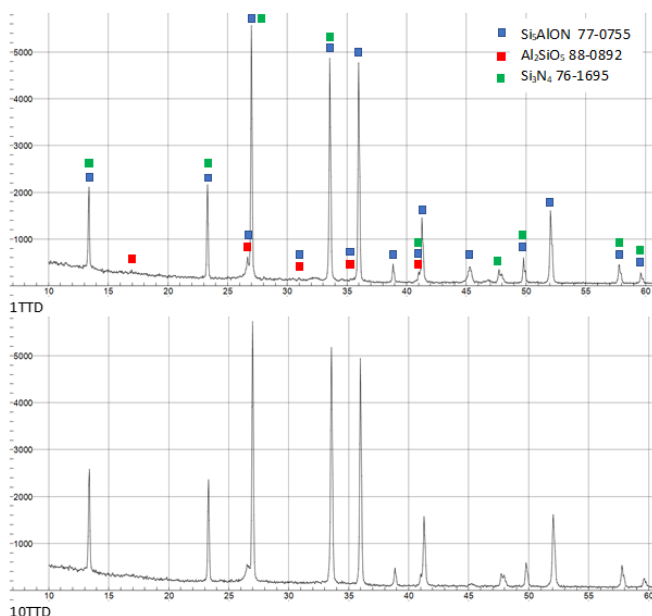


Fig.5. XRD results of the specimens (1TTD and 10TTD) cross-section after heat treatment in nitrogen.

The performed phase analysis did not reveal any significant differences in the composition of the samples after sintering. In this case, the addition of carbon nanotubes had no significant effect on the formation of new phases in the sialon system.

4. CONCLUSIONS

The application of ultrasonic dispersion, a nonpolar solution for dispersion, and a protective atmosphere during a sintering process (of nitrogen) maintained the structure of nanotubes in the tested composites after sintering. The low concentration of CNTs (1% weight) did not change the structure of the composites and only slightly worsened the sinterability of the nitride matrix. Mechanochemical activation of the nitride precursor enabled the production of low-porosity (5 vol%) Si₃N₄-CNT composites via pressureless sintering at 1600 °C. A larger content of CNTs (10 wt%) prevented the production of non-porous composites using this method due to mass transport by the gas phase, and changes to the microstructure of the composite made it difficult to obtain concentrated composites. It seems that shortening the nanotubes by reducing the *L/D* value could improve the microstructure, but the influence of this treatment on the functional properties is difficult to predict.

The applied dispersion methods for the nanotubes were insufficient, and clusters of fibers were observed in the microstructure. Catalyst residues, from the synthesis of the nanotubes, had an unfavorable influence on the mass transfer by the gas phase and on the crystallization of new fibers during the sintering of nitrogen ceramics. Applying pressure sintering, which should accelerate the sintering process at lower temperatures and limit the distribution of silicon nitride, may be an effective method. The hardness of tested samples remained at an expected level, which proves that adding carbon nanotubes to sialon ceramics can improve the mechanical properties of these ceramics.

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