Development of CNT-Silicon Nitrides with Improved Mechanical and Electrical Properties

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Abstract. This work is focusing on exploring preparing processes to tailor the microstructure of carbon nanotube (CNT) reinforced silicon nitride-based ceramic composites. Samples with different porosities and different amount (1, 3 or 5 wt%) of carbon nanotubes have been prepared by using gas pressure sintering or hot isostatic pressing. In comparison, composites with 1wt%, 5wt% or 10wt% carbon black and graphite have been manufactured. We measured the room temperature mechanical and electrical properties, examined the micro and nano structure by X-ray diffraction and electron microscopy. It was found that it is possible to develop CNT-silicon nitride composite for applications where a decent electric conductivity and good mechanical properties are required.

Introduction

The question of using carbon nanotubes (CNTs) as reinforcing phase in composites with different matrices is in the focus of materials science. As resulted from several theoretical calculations, CNTs are characterized by exceptional mechanical and electrical properties [1-3]. Therefore, it has been expected that their addition will radically improve the quality of various matrices. Ceramic composites containing CNT were produced on the base of alumina [4,5], silicon carbide [6] and silicon nitride [7,8]. The mentioned publications reported only modest improvements of properties. Surprising effects were observed the explanation of which seems to be rather obscure. Solving of two problems is inevitable for an effectual control the manufacturing of CNT/ceramic composites. It is necessary to disperse CNTs in the starting powder mixture and to preserve them during high temperature processing.

The aim of the present work is to develop sintering procedure which is suitable for tailoring the microstructure of multiwall carbon nanotube (MWNT) reinforced silicon nitride-based ceramic composites. Conventional sintering techniques gas pressure sintering (GPS) and hot isostatic pressing (HIP) were applied. Composites with carbon black and graphite additives have been also prepared to assist in understanding the micro and nano processes occurring during manufacturing. Not only the mechanical properties were determined but the electric conductivity, too. It is believed that a CNT- silicon composite having excellent thermal properties, good mechanical properties and a medium level electrical properties will meet with the wishes of market.
Experimental

Ceramic powder mixtures were prepared from Si₃N₄ (Ube, SN-ESP), Al₂O₃ (Alcoa, A16) and Y₂O₃ (H. C. Starck, grade C) powders, their share in all cases was 90%, 4% and 6%, respectively. The amount of added carbons was 1 – 10%. Trade name of carbon black was “Taurus Carbon black, N330” its particle size was between 50-100 nm. Synthetic graphite powder from Aldrich with particle size 1-2 µm were also used. Multiwall carbon nanotubes were manufactured in the Department of Applied and Environmental Chemistry of the University of Szeged [14]. Powder mixtures were milled in ethanol in a planetary type alumina ball mill for three hours, then the batches were dried and sieved. Green samples were obtained by dry pressing at 220 MPa using polyethylene glycol (PEG) as compaction agent. The following oxidizing heat treatment eliminated the PEG but preserved the carbon additive if the temperature - time run was appropriately chosen.

Samples prepared such a way were sintered in an ABRA made apparatus (Ceramic and Composites Laboratory, Budapest). Two step HIPing was performed in high purity nitrogen using BN embedding powder. In the first step samples were heated to a temperature about 1700°C, the pressure was 1.5 MPa. When the temperature was appropriate the pressure was increased to 20 MPa followed by 3 hours holding. In some cases high pressure was not applied, samples were heated as in the first step of HIPing then were cooled down. In this paper the second type of heat treatments is named gas pressure sintering (GPS).

Before mechanical testing all surfaces of samples were finely ground then the edges were chamfered. The dimensions of specimens were 3.5 x 5 x 50 mm. The elastic modulus and the four-point bending strength were determined with spans of 40 and 20 mm. DC conductivity was measured with four point contact using a high impedance multimeter (Agilent34970A) up to 10 MΩ overall termination. Samples with higher impedance showed overload in DC measurements, their impedance, however, could be measured by AC method [10].

Density of materials was measured by Archimedes method. Phase composition was determined by Bruker AXS D8 Discover X-Ray diffractometer using Cu Kα radiation. Morphology of the solid products was studied by field emission scanning electron microscope, LEO 1540 XB.

Results and discussion

Density. The addition of any carbon sort significantly decreased the rate of sintering (Table 1). A plausible explanation of this effect is to suppose that the added carbon located between ceramic particles hinders the generation and growth of interparticle contacts. The driving force of sintering is the decrease of surface energy of ceramic particles, therefore a reduction of the rate is normal. It can be assumed that the larger is the coverage of ceramic particles the stronger is the retardation. The coverage depends on the amount and size of hindering phase, other effects such as the strength of ceramic-carbon and carbon-carbon bonds also play important role.

Measured data reflected the complexity of phenomenon (Table 1). In all cases samples containing CNT had smaller density than graphite or CB containing ones. When the amount of additive was 1% relatively small differences between densities of the three category of GPS samples were observed. The specific features of carbon additives clearly revealed when 5% carbon was added. HIP treatment could enlarge the density when the amount of additive was 1 or 3%, but could not when it was 5%.
Table 1 Density of samples after gas pressure sintering and HIPing as a function of sort and amount of added carbon

<table>
<thead>
<tr>
<th>Sintering</th>
<th>Additive</th>
<th>Amount [wt.%]</th>
<th>0</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPS</td>
<td>Graphite</td>
<td>Density [g cm(^{-3})]</td>
<td>3.072</td>
<td>2.840</td>
<td>2.742</td>
<td>2.742</td>
<td>2.429</td>
</tr>
<tr>
<td>GPS</td>
<td>Carbon black</td>
<td></td>
<td>2.893</td>
<td>2.381</td>
<td>2.029</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GPS</td>
<td>Carbon nano tube</td>
<td></td>
<td>2.807</td>
<td>2.653</td>
<td>2.240</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HIP</td>
<td>Graphite</td>
<td>3.225</td>
<td>3.178</td>
<td>2.723</td>
<td>2.875</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HIP</td>
<td>Carbon black</td>
<td>3.198</td>
<td>2.410</td>
<td>2.163</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HIP</td>
<td>Carbon nano tube</td>
<td></td>
<td>3.028</td>
<td>2.752</td>
<td>2.245</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Mechanical properties.** Figure 1 and Figure 2 show the four point strength of samples after GPS and HIP, respectively. In the case of gas pressure sintering several temperature-time runs were executed, the goal was to cover a wide porosity range. In this case it is possible to distinguish between two density ranges (Fig. 1). When the density was lower than 2.5 g cm\(^{-3}\) the strength depended only on the density, while at higher densities the addition of CNT gave higher values than the addition of graphite or carbon black.

We did not obtain clear picture about the effect of hot isostatic pressing (Fig.2). A part of the samples had open porosity when the pressure was increased, therefore both density and strength were similar to their values obtained by GPS. The scatter of results is rather high because the applied process was worked out for silicon nitride ceramics, not for CNT-silicon nitride composites. The perspective is not bad, 400-500 MPa four point strength was obtained even without the application of high pressure (Fig. 1), compared with 700-850 MPa of silicon nitride ceramics.
Figure 2. Four point strength as a function of the apparent density after hot isostatic pressing

**Electrical properties.** The silicon nitride base ceramics are isolators, their specific conductivity is about $10^{-12}$ S m$^{-1}$. According to our measurements all composites containing 1% additives were also isolators. At higher additive content the conductivity strongly depended on the sort of addition. The effect of graphite was weakest, conductivity can not be detected in samples when its amount was 5%. In the case of 10% graphite additive a part of samples was isolator, another part had a conductivity about 0.3 – 1 S m$^{-1}$. Addition of 5% - 10% carbon black, or 3 –5% carbon nanotube resulted in materials having 1 – 1700 S m$^{-1}$ electrical conductivity.

Fig.3 shows the measured conductivity as a function of density, carbon black gave higher values than nanotube. The conductivity of GPS samples increased with increasing additive content in series BC 1-5-10 and G5 – 10. In the case of HIPed carbon nanotubes (series CNT 3 – 5) the opposite trend was observed. The application of high pressure (20 MPa) decreased the conductivity of BC 5 sample, the BC 10 sample and the CNT5, but increased that of G10.

**Structure.** The amount of β phase comparing with the sum of α and β phases is shown in Fig 4. In the case of GPS no difference between ratios of samples containing CNT and another ones could be observed. The development of β phase occurred in CNT samples before the closure of pores at density 2.7 g cm$^{-3}$ (83% of the theoretical value), while in silicon nitride ceramics this phase transformation started after the closure of pores at about 2.95 g cm$^{-3}$ (91%) [11,12].

The micro and nano structure of CNT-silicon nitride composites were examined by scanning and transmission electron microscopy [7,10,13]. The observations proved that the carbon nanotubes had a good adherence to the silicon nitride grains. If CNTs were dispersed in the starting powder mixture and the sintering parameters were properly designed the majority of nanotubes were
located on grain boundary surfaces [8, 10, 13]. Tendencies of the variation of measured mechanical and electrical properties can be explained by the strong bond between CNT and ceramic particles. The next step is to determine exact relationships between processing parameters and properties.

Figure 3. Specific conductivity as a function of apparent density

Figure 4. The amount of beta phase as a function of apparent density
Conclusions

The addition of carbon nanotube or graphite or carbon black significantly decreased the rate of sintering due to blocking the ceramic-ceramic contacts. The feature of density – strength relationship altered at about 2.5 g cm\(^{-3}\). The addition of carbon nanotube resulted in elevated strength above this density. The composite is electrically conductive when 3% carbon nano tube is added. It is possible to develop CNT-silicon nitride composite having decent electric conductivity and good strength simultaneously. Actual values are 10 S m\(^{-1}\) and 450 MPa.

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