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Short communication

The effect of milling time on the sintering kinetics of Si_3N_4 based nanocomposites

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Abstract

Multi-walled carbon nanotube (MWCNT) reinforced silicon nitride composites have been prepared by hot isostatic pressing at 20 MPa and gas pressure sintering at 2 MPa. To assure a good dispersion of the MWCNTs a highly efficient attritor milling was employed in the preparation process of the powder mixtures. The morphological and micro-structural evolution of the powder particles during the high-energy milling was monitored.

We have found that the milling time has a complex influence on the structure and mechanical properties of the resulting nanocomposites through affecting both the dispersion and degradation of the nanoscale filler as well as the phase transformations of the ceramic host.

Keywords: A. Sintering; B. Nanocomposites; C. Mechanical properties; Ceramics; Carbon nanotubes

1. Introduction

Carbon nanotubes (CNTs), discovered by Ijima, during their twenty-years history have shown to possess remarkable mechanical, electrical and thermal properties, therefore, they are intensively studied as reinforcing agents in ceramic matrix composites [1–7]. One of the most important requirements for nanocomposites is to provide a homogeneous distribution of the reinforcing phase. If the reinforcement particles tend to agglomerate, the mechanical and electrical properties of the composite will be deteriorated.

Several different methods have been developed to improve the dispersion. CNT-reinforced ceramic composites were realized [8] by using polymer derived ceramics (PDCs), which assures the desired dispersion grades in liquid-phase precursors just before the pyrolysis. A colloidal processing as an efficient dispersing tool has also been proposed [9]. However, probably the simplest way to improve the dispersion is the milling of nanoscale fillers together with the precursor powders. Unfortunately the milling method is not also the most efficient for dispersing the nanoscale fillers; further optimization is needed in this direction. A dry ball-milling technique was proposed to improve the particle distribution [10]. High-energy milling has also been used [11] to disperse silicon-nitride particles in aluminum powder, as well as to prepare Al_2O_3 and SiO_2 ceramics [12].

For Si_3N_4/CNT nanocomposites we have already developed a method consisting of highly efficient ultrasonic agitation and milling process, combined with the functionalization of carbon nanotubes [13–15] to achieve a good dispersion of nanotubes in silicon nitride ceramics. However, several works reported that the milling time, milling atmosphere and the type of the mill also have important influences on the morphology and microstructure of the starting powder [16–18] and consequently the properties of the resulting composites [19]. Therefore, we have investigated the effect of milling time on mechanical properties of carbon nanotubes reinforced silicon nitride ceramics prepared at different sintering conditions.

To properly understand the correlation between structure and properties, scanning electron microscopy (SEM) measurements have been involved to investigate the morphology and microstructure, both of the milled starting powder and the sintered samples. However, apart from the size and morphology of the starting powder, phase changes during sintering can also play an important role in the properties of the resulting nanocomposites. In order to monitor the sintering kinetics of our samples, X-ray diffraction (XRD) measurements have been performed to reveal possible phase transformations during the

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Table 1
Composition, preparation conditions, and apparent densities of the sintered samples.

Samples	CNT addition (wt%)	Milling time (h)	Sintering pressure (MPa)	Apparent density (g/cm^3)
GPS-1	3	1	2	2813
GPS-3	3	3	2	2825
GPS-5	3	5	2	2983
HIP-1	3	1	20	3092
HIP-3	3	3	20	3171
HIP-5	3	5	20	3330

sintering. The mechanical properties of the ceramics have been characterized by three-point bending strength measurements using an INSTRON-1112 tensile/loading machine.

2. Experimental procedure

The composition of the starting powder mixtures and some details about preparation methods are presented in Table 1. Starting powders used in our experiments were as follows: 90 wt% Si_3N_4 (Ube, SN-ESP); as sintering aids we used the following powders: 4 wt% Al_2O_3 (Alcoa, A16) and 6 wt% Y_2O_3 (H.C. Starck, grade C). The powder mixtures together with MWNTs (produced by CCVD method described in details in [14]) were milled in distilled water in high efficiency attritor mill (Union Process, type 01-HD/HDDM) with high rotation speed, 4000 rpm (circumferential speed of ~20 m/s). Polyethylenglycol (PEG) was added to the powder mixtures. The batches were sieved with 150 μm mesh. Green samples were obtained by dry pressing at 220 MPa. Samples prepared for HIP were oxidized at 400 °C to eliminate the PEG. Hot isostatic pressing (ABRA type) (HIP) was performed at 1700 °C in high purity nitrogen using BN embedding powder at 20 MPa, with 3 h holding time. Gas pressure sintering (GPS) at 2 MPa was performed at 1700 °C, 2 MPa nitrogen pressure, without holding time. The heating rate did not exceed 25 °C/min. The dimensions of the as-sintered specimens were 3.5 mm × 5 mm × 50 mm.

The density of the sintered materials was measured by the Archimedes method. Phase compositions were determined by Philips PW 1050 X-ray diffractometer. Morphology of the solid products was studied by field emission scanning electron microscope, LEO 1540 XB. The three-point bending strength values for both HIP and GPS samples were determined by bending tests on an INSTRON-1112 tensile/loading machine with spans of 20 mm, by measuring three samples for each milling time and sintering pressure.

3. Results and discussion

To study the effect of the milling time as a first step we have investigated the morphology of powder mixtures processed

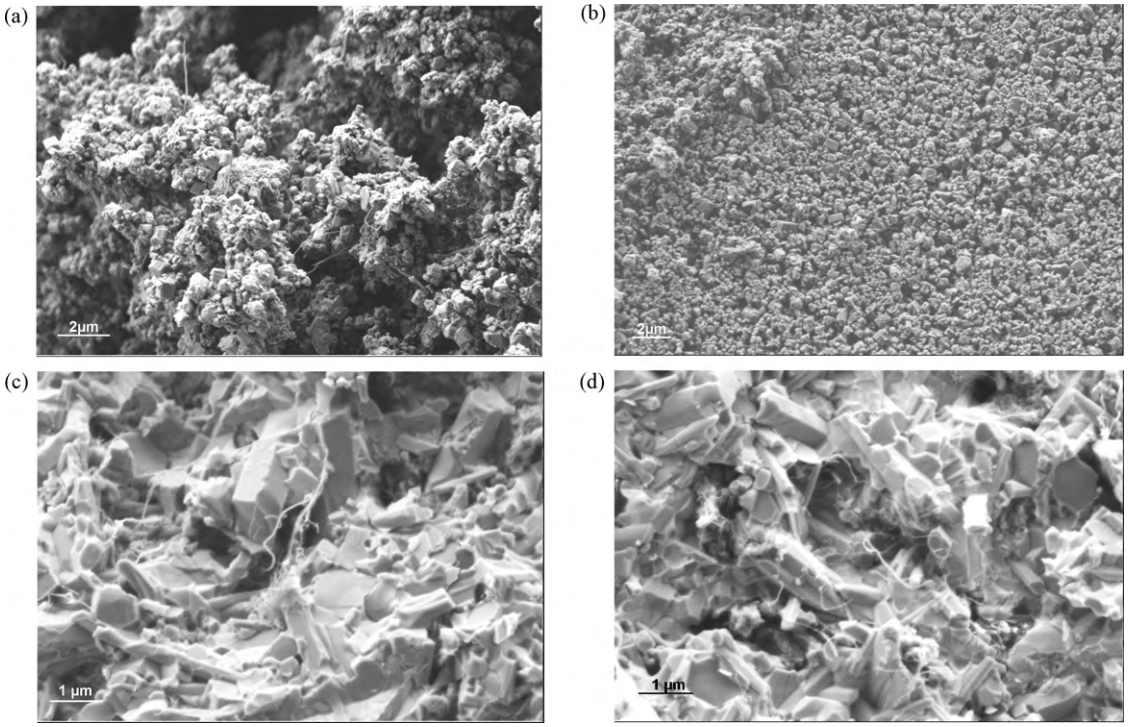

Fig. 1. SEM images of starting powder mixtures prepared with different milling times: (a) 1 h and (b) 5 h. SEM images of fracture surfaces of samples, sintered at 2 MPa (c) and 20 MPa (d) gas pressure, prepared with 5 h milling time.

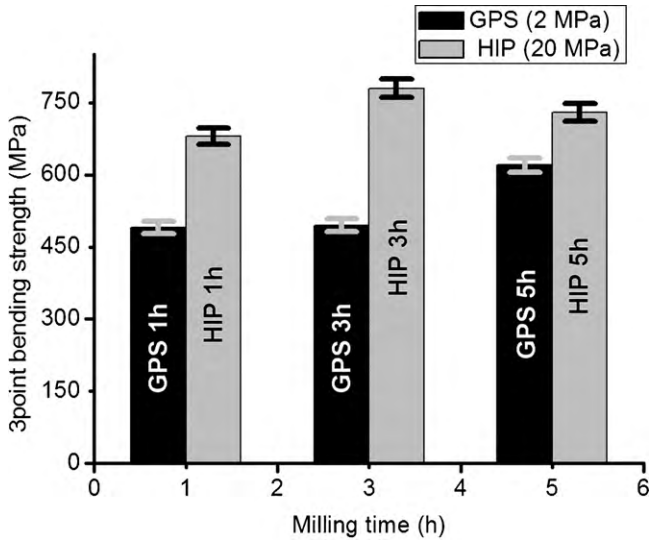

Fig. 2. Three-point bending strength of the nanocomposites as a function of milling time, for the case of samples sintered at 2 MPa (GPS) and 20 MPa (HIP) pressure.

with different milling times in the attritor mill by scanning electron microscopy (SEM).

The morphology of the starting powders with MWCNTs milled for one, respectively five hours are presented in Fig. 1a and b. Conform to expectations by increasing the milling time smaller particle size and narrower particle size distribution has been achieved.

The X-ray diffraction measurements showed that the starting powder mixtures mainly contains α-Si_3N_4.

In order to investigate the morphology of sintered samples scanning electron micrographs of fracture surfaces of samples with 3% MWCNTs prepared at 2 MPa (c) and at 20 MPa (d) were taken, as can be seen in Fig. 1. Although degradation of nanotubes may occur during high temperature sintering [3,8], after optimizing our preparation process the CNTs are preserved in the matrix as can be seen in the SEM images. The proper separation and dispersion of carbon nanotubes proved to be a difficult step of the composite preparation. To achieve a better dispersion, we applied a highly efficient attritor mill. However, some agglomeration of the CNTs, located mainly in the inter-granular places [20], still can be observed on the scanning electron micrographs. Due to this drawback only our best samples reach the mechanical properties of the reference samples prepared without CNT addition, however, our composites containing CNTs, beside preserving the good mechanical properties of silicon nitride ceramics, are also good conductors of electricity and heat [21]. In order to investigate the mechanical properties of the nanocomposites, we have measured their three-point bending strength as a function of milling time (Fig. 2).

Increasing the milling time up to a limit results in improved mechanical properties (Fig. 2). However, further increasing the milling time can lead to the deterioration of mechanical properties as indicated by 3 point bending strength measurements on HIP samples (Fig. 2), which shows a slightly decreasing bending strength for the samples milled for 5 h as

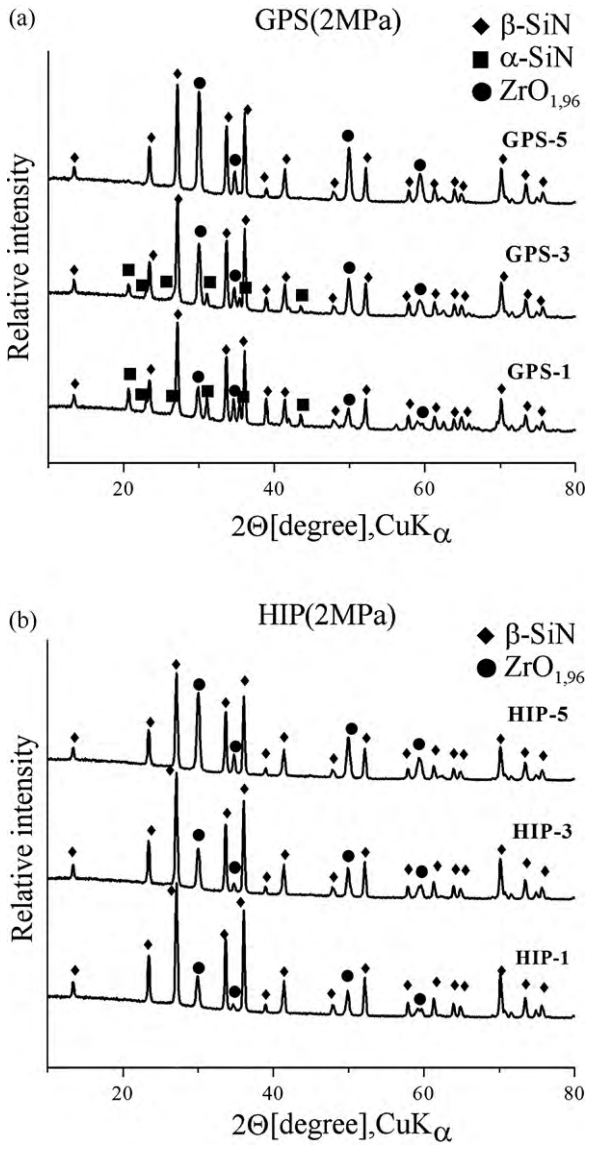

Fig. 3. X-ray diffractograms of sintered samples containing 3 wt% MWCNTs, prepared by GPS (a) and HIP (b).

compared to the one milled for 3 h. Since in this time range the grain size of the powder still decreases (and consequently the density of the sintered samples still increased) with increasing milling time. We attribute the lack of improvement in mechanical properties to the deterioration of the filler carbon nanotubes phase. Although the SEM images of fracture surfaces are not suitable to directly reveal the structure of carbon nanotubes, it is known that milling the samples for long times is likely to induce serious damages in the structure of CNTs [22].

In contrast, for the case of samples sintered at 2 MPa the samples milled for 5 h show the highest bending strength. To get insight into the distinct mechanical behavior of samples sintered at different conditions we have also investigated the phase composition of the ceramics, as a function of the milling time and sintering parameters (Fig. 3). X-ray diffractograms of sintered samples are presented in Fig. 3. The main lines of α-

Si_3N_4 (JCPDS-PDF 41-0360), β-Si_3N_4 (JCPDS-PDF 33-1160) and $ZrO_{1.96}$ (JCPDS-PDF 81-1546, contamination from the milling balls) lines can be recognized.

In the case of samples sintered at 20 MPa, (HIP) a complete α-Si_3N_4 to β-Si_3N_4 phase transformation is revealed for all milling times as can be seen in Fig. 3b.

However, in the case of samples sintered at 2 MPa (GPS), the samples milled for 1 and 3 h contain both α and β silicon nitride phases. While in the case of the sample milled for 5 h the α-Si_3N_4 to β-Si_3N_4 phase transformation was completed (Fig. 3a, GPS-5). Therefore, at 2 MPa sintering pressure (contrary to 20 MPa) the substantial improvement of mechanical properties between samples milled for 3 respectively 5 h can be attributed to the phase transformation of the matrix, which in this case (lower sintering pressure) is also dependent on the grain size of the starting powder, consequently on the milling time.

This result shows that beside the well known effects of milling time on grain size, and dispersion (and degradation) of carbon fillers, its effect on sintering kinetics (i.e. phase transformations of the matrix material) can also play an important role in determining the mechanical properties of the silicon nitride/CNT nanocomposite under certain sintering conditions.

4. Conclusions

We have studied the effect of milling time on mechanical properties of Si_3N_4/MWCNT nanocomposites. We have shown that by increasing the milling time up to a limit the mechanical properties of the Si_3N_4/CNT nanocomposites can be improved. This is mainly due to the increasing of the final density (due to the smaller grain size of the starting powder) and the improving dispersion of the nanotubes with longer milling times. Further increase in milling time can result in the degradation of mechanical properties due to the degradation of the filler phase. Furthermore, by XRD measurements we showed, that the phase transformation of the matrix material (α-Si_3N_4 to β-Si_3N_4), is also dependent on milling time at low sintering pressures (2 MPa) while it is always complete for higher sintering pressures (20 MPa). Best results can be achieved by intermediate milling times (∼3 h) which assures a high enough final density and good nanotube dispersions, but preserves the mechanical properties of nanotubes. Furthermore, for best results, the as prepared powders have to be sintered at high enough pressures for the α-Si_3N_4 to β-Si_3N_4 phase transformation to complete. On the other hand if lower sintering pressures are applied the milling time should be increased to achieve the better mechanical properties.

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