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Effect of single-walled carbon nanotubes on thermal and electrical properties of silicon nitride processed using spark plasma sintering

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Abstract

Si_3N_4 nanocomposites reinforced with 1-, 2-, and 6-vol% single-walled carbon nanotubes (SWNTs) were processed using spark plasma sintering (SPS) in order to control the thermal and electrical properties of the ceramic. Only 2-vol% SWNTs additions were used to decrease the room temperature thermal conductivity by 62% over the monolith and 6-vol% SWNTs was used to transform the insulating ceramic into a metallic electrical conductor ($92\,S\,m^{-1}$). We found that densification of the nanocomposites was inhibited with increasing SWNT concentration however, the phase transformation from α- to β-Si_3N_4 was not. After SPS, we found evidence of SWNT survival in addition to sintering induced defects detected by monitoring SWNT peak intensity ratios using Raman spectroscopy. Our results show that SWNTs can be used to effectively increase electrical conductivity and lower thermal conductivity of Si_3N_4 due to electrical transport enhancement and thermal scattering of phonons by SWNTs using SPS.

Keywords: Single-wall carbon nanotubes; High-temperature materials; Thermal properties; Electrical properties; Composites

1. Introduction

SWNTs are considered to be ideal fiber reinforcements for the creation of multifunctional nanocomposites with enhanced fracture toughness and strength, and enhanced electrical and thermal conductivities in polymeric, ceramic, and metallic based nanocomposites.[1–4] SWNTs possess exceptional mechanical ($E > 1$ TPa and TS > 7 GPa)[5] thermal ($k \sim 1750$–$5800\,W\,m^{-1}\,K^{-1}$),[5–7] and electrical properties ($\sigma \sim 10^6\,S\,m^{-1}$)[5,8] and have considerably high aspect ratios (1,000 up to 10,000) that are critical for their use in the design of nanocomposites. SWNTs have high electrical conductivity along the tube axis and depending on the type of the arrangement of bond structure chirality within the nanotube, a SWNT can be either metallically conducting or semiconducting. Experimental results show that a SWNT rope has a longitudinal electrical conductivity of $10^6\,S\,m^{-1}$ at 300 K.[5,9] Theory predicts high thermal conductivity values ($5800\,W\,m^{-1}\,K^{-1}$) for the room temperature longitudinal thermal conductivity of an individual SWNT.[7] However, experimental measurements of aligned bundles of SWNTs showed a measured thermal conductivity of only $250\,W\,m^{-1}\,K^{-1}$ at room temperature.[8] Although, SWNTs have high thermal conductivity, it is very difficult to realize this effect in a composite. This is mainly because SWNTs are not continuous throughout the bulk composite. Therefore, they create more interfacial defects, which may lower the lattice thermal conductivity. In addition, depending on the SWNT synthesis method, lot-to-lot variability, chirality of the structure, defects, and single vs. bundles of SWNTs there are a number of additional variables that make it difficult to fully understand the effect of SWNTs on thermal and electrical properties when used as additives in nanocomposites. Clearly, ongoing efforts focused on enhancing the production quality, length scale, chiral structure and defects, and quantity of SWNTs[9–12] will

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help promote an understanding of their effects in nanocomposite systems. Once, continuous and uniform SWNTs are processed into a composite will the potential for enhanced thermal conductivity properties be realized and may lead to the use of SWNTs for high-performance thermal management systems.

The vast majority of SWNT nanocomposites have been focused on polymeric systems due to favorable processing methods that allow chemical handling of each material at room or low temperature conditions. However, for both metal and ceramic nanocomposite development the challenge lies with incorporating SWNTs at high temperature either though conventional melting casting or sintering methods. This becomes a significant hurdle to overcome when SWNTs are not stable at high temperatures >600 °C (in air)[13] and oxidize. Therefore, exposing SWNTS to extreme temperatures (>1800 °C) and pressures (50 MPa) using conventional ceramic sintering methods puts them at higher risk for oxidation and structural damage. The challenge for researchers to process SWNTs in high-temperature ceramic matrices such as, carbides, nitrides, and borides, is primarily during sintering where temperature requirements usually exceed 1800 °C, using conventional sintering methods.[14–16] In addition, creating processing methods that enable homogeneous dispersions of SWNTs and ceramic particles is critical for obtaining uniform densification and physical properties of the ceramic nanocomposites. The most promising method for dispersing SWNTs in a ceramic is to use colloidal processing in order to manipulate interparticle pair potential in order to create homogeneous aqueous or solvent based dispersions of powders and SWNTs. Our previously published work[14] and work published by others[17–19] has shown that colloidal processing methods are highly effective in obtaining well dispersed homogeneous SWNTs in oxide and non-oxide ceramics. The basis for this approach is to treat the ceramic particle and the SWNT as a colloid particle and employ conventional colloidal processing methods that involved manipulating the inter-particle and inter-tube pair potentials.[20]

Despite the processing challenge presented by creating ceramic nanocomposites and the variability between individual and bundles of SWNTs there have been promising results for oxide and non-oxide based SWNT ceramic nanocomposites. Recent work by others and us shows the potential to enhance toughness of brittle ceramics and to tailor their electrical and thermal conductivity properties.[4,16,21–24] For example, the SWNT–Al_2O_3 nanocomposites processed using SPS and conventional ceramic powder mixing/blending methods have shown to increase fracture toughness by 30%,[22] while also creating a metallic electrically conductive ceramic with anisotropic thermal properties.[23] In addition, Balani et al.[25,26] enhanced the fracture toughness of alumina by 42% over the monolith. Recently, the work by Zhang et al.[19] has shown for the first time that pressure-less sintering can be used to densify and consolidate MWNT-Al_2O_3 nanocomposites at 1500 °C for 2 h and obtain ∼99% theoretical density without detectable damage to the MWNT structure. Their results also show modest enhancements to fracture toughness due to pull out of the MWNTs and significant increases in flexural strength over the monolith. Recently, Inam et al.[27] reported that using 5-wt% MWNTs in Al_2O_3 they were able to create excellent electrical conductors with conductivity values greater than 500 S m^{-1}.

However, there has been limited success in creating ceramic nanocomposites with significant enhancements to thermal conductivity, which is an important physical property that helps us understand how heat transfers through a solid. Bakshi et al.[28] were able to enhance the thermal conductivity of Al_2O_3 coatings using 4-wt% MWNTs. Also, Sivakumar et al.[29] reported a 70% increase in thermal conductivity of SiO_2 using 10-vol% MWNTs. However, the improvements they measured fall short of the enhancements predicted by rule of mixtures calculations. On the other hand, Zhan et al.[21] observed a decrease in thermal conductivity with increasing vol% SWNT. There are a number of reasons for the lower thermal conductivity values that take into consideration that SWNT bundles have lower thermal conductivity values than individual SWNTs and that the number of interfaces between the Al_2O_3 and the SWNTs creates high thermal resistivity thus limiting thermal conduction in the nanocomposites. It is also important to note that residual porosity within the ceramic nanocomposite also serves to scatter phonons and limit thermal conduction within a ceramic.

Our previous work shows we can enhance the fracture toughness of Si_3N_4 by 30% upon optimization of SWNT concentration (2-vol% SWNT) and SPS temperature (1600 °C).[14] In addition, others have published results for MWNT reinforced Si_3N_4 showing that for high concentrations of MWNTs (>4 wt%) they react to form SiC thus decreasing the density of the nanocomposite. However, using a lower concentration of MWNTs they were able to maintain the high strength and toughness of the monolith.[16] Thus, the main challenge with processing non-oxide based MWNT or SWNT reinforced ceramic nanocomposites in addition to dispersion of the nanotubes is achieving high density after high-temperature and high pressure assisted sintering. Furthermore, Balazsi et. al.[30] processed MWNT based Si_3N_4 nanocomposites using SPS and hot-pressing and report that the SPS method is superior to hot-isostatic pressure assisted sintering method in obtaining high density and MWNT damage-free structures in Si_3N_4. They also created MWNT–Si_3N_4 nanocomposites with electrical conductivity values greater than 100 S m^{-1}. Recently, SPS has been shown to be a very powerful tool to develop functionally graded and MWNT based nanocomposites. Belmonte et al.[31] have shown that they can process high density nanocomposites and show that SPS can be used to limit MWNT degradation at temperature and that SPS is a powerful tool to develop silicon nitride with controlled microstructures.[32]

The goal of this paper is to investigate the effect of SWNTs on the electrical and thermal properties of Si_3N_4 after densification using SPS. The purpose of the manuscript is to discuss the effect of SPS temperature on SWNT stability at high-temperatures (>1700 °C) and demonstrate that our approach that uses colloidal processing and SPS is successful in retaining pristine and dispersed SWNTs in the sintered microstructure that allow for the enhancement and decrease of the electrical and thermal conductivity properties, respectively.