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Mechanical properties and electrical conductivity in a carbon nanotube reinforced silicon nitride composite

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Abstract

The influence of carbon nanotubes (CNTs) addition on basic mechanical, thermal and electrical properties of the multiwall carbon nanotube (MWCNT) reinforced silicon nitride composites has been investigated. Silicon nitride based composites with different amounts (1 or 3 wt%) of carbon nanotubes have been prepared by hot isostatic pressing. The fracture toughness was measured by indentation fracture and indentation strength methods and the thermal shock resistance by indentation method. The hardness values decreased from 16.2 to 10.1 GPa and the fracture toughness slightly decreased by CNTs addition from 6.3 to 5.9 MPa $m^{1/2}$. The addition of 1 wt% CNTs enhanced the thermal shock resistance of the composite, however by the increased CNTs addition to 3 wt% the thermal shock resistance decreased. The electrical conductivity was significantly improved by CNTs addition (2 S/m in 3% Si_3N_4/CNT nanocomposite).

Keywords: C. Electrical conductivity; C. Mechanical properties; C. Thermal shock resistance; Si_3N_4–CNT composites

1. Introduction

Silicon nitride has very good combination of mechanical, physical, and chemical properties. The strength, hardness, and toughness at room and elevated temperatures make it suitable for use in several structural applications [1]. To obtain superior mechanical properties, a fine-grained microstructure with elongated beta grains is preferred. These in situ grown beta silicon nitride grains can significantly improve the fracture toughness over monolithic ceramics, producing self-reinforced silicon nitrides [2]. Ex situ toughening of silicon nitrides is also accomplished with the addition of fibers such as SiC and carbon [3,4].

Carbon nanotubes (CNTs) offer new possibilities to improve the functional and mechanical properties of advanced ceramics thanks to their small size, large aspect ratio, low mass and excellent mechanical, electrical and thermal properties [5,6]. For high-temperature applications, the high thermal conductivity of CNTs suggests that their incorporation, even at low volume fraction, might provide the thermal transport needed to reduce material operating temperatures and improve thermal shock resistance [7]. Such composites may find applications in catalyst supports, hydrogen storage, electrodes for fuel cells, supercapacitors, and ultrafiltration membranes. During the last decade new ceramic/carbon nanotube composites have been developed and a number of authors have reported improved mechanical and functional properties in the case of ceramic/CNT composites compared to the monolithic material [8–16]. Three main problems have been recognized during these investigations: dispersion of the CNTs in the matrix, densification of the composites and degradation of the CNTs [17–20].

An increase of the fracture toughness and of electrical conductivity has been achieved in CNTs reinforced alumina matrix composites, but only modest improvements of electrical and mechanical properties were found in carbon nanotube silicon carbide-, polymer-, metal oxide matrix composites [21–24]. CNT-CMC materials have demonstrated significant enhancements in electrical conductivity at relatively low CNT volume fractions. It was reported that CNT-dispersed Al_2O_3 fabricated by the spark plasma sintering (SPS) method, which is one of the densification techniques at low

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temperatures, had extremely high fracture toughness, because of the bridging effect of CNTs [25]. Furthermore, the strength of these materials is degraded by CNT dispersion due to insufficient densification, although CNTs should improve the mechanical properties. CNT dispersed silicon nitride composites have been made by Balázsi et al. [26] with improvements in strength, stiffness, and toughness. Tatami et al. [9] developed CNT dispersed Si_3N_4 ceramics with high density, electrical conductivity, and superior mechanical properties by using novel sintering aids (Y_2O_3–Al_2O_3–TiN–AlN).

Most work on CNT-CMCs has focused on the measurement of toughness using the indentation/crack length technique but most results for toughening have been disappointing. Data has shown very little or no increase in toughening upon introduction of CNTs – either single- or multi-walled – into various ceramic matrices [21,27,28]. Toughening has been obtained through the toughening mechanisms e.g. crack bridging by CNTs, crack deflection at CNT/matrix interface and nanotube pull-out on the fracture surface [1,29]. The mechanical properties strongly depend on the type of nanotubes, as well as nanotube/matrix interactions [26].

Recently, different investigations have been focused on the study of the grain boundaries in different CNTs/CNFs reinforced ceramic composites [30–33]. Vasiliev [30,31] based on the results of transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HREM), presented a new way of perceiving grain boundaries in alumina/SWCNTs composite. Balázsi [32] investigated the interface between the beta-Si_3N_4 crystallites and MWCNTs by TEM and HREM in the composites based on silicon nitride and reinforced by 1 and 3 wt% of MWCNTs. Kothari et al. [33] during investigation of the effect of MWCNTs and dense as received and heat treated CNFs on the reinforcement in amorphous silicon nitride coatings, found that the heat treatment of CNFs changed the character of the CNT/matrix interface and increased the pull-out. Significantly longer pull-out was found however in the case of MWCNTs.

However, only few researchers [11] have been concerned with thermal properties of carbon nanotube composites in ceramic systems. The thermal shock resistance of brittle materials generally depends on a number of thermal and mechanical properties mainly thermal expansion coefficient, thermal conductivity, thermal diffusivity, Young's modulus, fracture toughness, strength, heat transfer coefficient, specimen size and duration of the thermal shock. Several thermal shock parameters have been defined to relate these materials to their thermal resistance, considering the crack initiation (R parameter) and crack propagation (R'''' parameter) conditions, respectively. They are defined as following [34]:

$$R = \frac{\sigma_c(1-\upsilon)}{\alpha E} = \Delta T_c \quad (1)$$

$$R'''' = \left(\frac{K_{IC}}{\sigma_r}\right)^2 (1+\nu) \quad (2)$$

where σ is the tensile strength, E the Young's modulus, α the coefficient of thermal expansion, K_{IC} is fracture toughness and ν is the Poisson's ratio.

Higher values of R represent greater resistance to fracture initiation during quenching and higher values of R'''' indicate less crack propagation once the critical temperature drop ΔT_c, necessary to initiate fracture, is exceeded.

In convectional testing thermal shock resistance is quantified by measuring of residual strength of polished specimens after quenching. This standardized method requires a large number of prepared (at least 30 samples) and it cannot allow multiple shock measurements. For these reasons an alternative indentation-quench method has been developed by Andersson and Rowcliffe [35]. In this technique, the thermal shock resistance is measured by studying the propagation of median/radial cracks around a Vickers indentation after single or repeated quenching. The critical temperature difference $\Delta T_{c\ ind}$, of the material can be defined with reference to the number of propagating cracks and the amount of crack extension.

The thermal shock resistance of Si_3N_4/CNTs composites has not yet been reported, but many authors have studied thermal shock resistance of different ceramic materials by water quenching or indentation tests (silicon nitride, silicon carbide, β-sialons, alumina/silicon carbide nanocomposites, etc.) [36–40].

The aim of the present contribution is to investigate the influence of the carbon nanotubes (CNTs) addition on the hardness, fracture toughness, thermal shock resistance and electrical conductivity of multiwall carbon nanotube (MWNT) reinforced silicon nitride composites.

2. Experimental materials and methods

2.1. Starting material and experimental setup

Some details about composition of the starting powder mixtures and preparation can be seen in Table 1. Si_3N_4 (Ube, SN-ESP), Al_2O_3 (Alcoa, A16) and Y_2O_3 (H.C. Starck, grade C)

Table 1
Starting compositions and preparation conditions of sintered samples.

Samples	Starting powders (wt%)			CNT (MWNT) (wt%)	Ball milling (wt%)	Ultrasonic agitation (wt%)	Sintering conditions		
	Si_3N_4	Al_2O_3	Y_2O_3				Temp. (°C)	Holding time	Pressure (MPa)
SN	90	4	6	–	3 h	–	1700	3 h	20
SN-CNT1	90	4	6	1	3 h	3 h (mixture + MWCNT)	1700	3 h	20
SN-CNT2	90	4	6	3	3 h	3 h (mixture + MWCNT)	1700	3 h	20