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Microstructure-toughening relation in alumina based multiwall carbon nanotube ceramic composites

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Abstract

Composites incorporating 0.0, 1.1, 6.4 and 10.4 vol.% of multiwall carbon nanotubes (MWCNTs) in alumina were processed by the spark plasma sintering. The effects of MWCNT contents on the fracture toughness, bending strength, hardness, elastic modulus were evaluated and potential toughening mechanisms were scrutinized. The fractured surfaces exhibit a new microstructure in which MWCNTs are positioned not only at the grain boundaries but also within the alumina grains. The observed longer and shorter pulled out lengths are generally commensurate with the corresponding thermal residual stresses residing at inter- and transgranular positions of alumina. The nanotubes protruding from inside alumina grains indicate the activation of classical fiber pullout induced toughening corroborated by the pullout induced residual holes observed first time in the composites. Meanwhile, nanotubes at the grain boundaries suggest the existence of stretching/disentangling toughening. The significant improvement in the toughness implies that there is a synergy between the two mechanisms.

Keywords: Mechanical properties; Alumina; Carbon nanotubes; Composite; Toughness and toughening

1. Introduction

The exceptional electrical, mechanical and thermal properties of carbon nanotubes (CNTs) have spurred extensive research activity in designing high performance ceramics based composites during the last ten years.[1,2] Alumina is a key structural material that has several applications in diverse fields such as, armor systems, wear resistance products, electronic substrates, cutting tools, automotive parts, components for power generator, turbine hot section, and aero-engine.[3–6] Despite much effort, the low fracture toughness has been continued not only the bane of alumina but also a source of its mechanical unreliability. Therefore, the high brittleness value of alumina limits its performance for some advanced applications.

Several attempts were made to improve mechanical reliability, especially the toughness of alumina by incorporation of carbon nanotubes.[7–9] Zhan et al. [10] investigated single wall carbon nanotubes (SWCNTs) as a nanoscale reinforcement in alumina and reported almost three fold improvements in the fracture toughness of the composite over pristine alumina. However, subsequent work demonstrated that the results were overestimated by the Vickers test.[11,12] Since the accommodation of shear deformation by carbon nanotubes severely limits cracking around the indenter that result in a highly augmented value of toughness in the composite.[11–13] In addition, the improvements were not substantiated by key evidence of potential toughening mechanisms. Therefore, the importance of standardized test for real estimation of toughness enhancement has been emphasized and it is widely agreed that the improvements must be corroborated by the key evidence of toughening mechanism in the composites. [11,12,14,15]

Todd and coworkers[15] investigated mechanical reinforcement of MWCNTs in alumino-borosilicate glass ceramic.

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Significant improvements in the mechanical properties were reported despite the fact that no substantial nanotube pull-outs of broken section were observed in their composites. Peigney et al. [16] conducted extensive work on preparation-microstructure-property relationships in double-walled carbon nanotube/alumina composites. The improved fracture strength was associated with the large scale crack bridging by less damaging carbon nanotubes.[16] Very recently they reported high fracture toughness in the MWCNT/alumina composite and enhancements were attributed to the crack bridging by non-covalent functionalized carbon nanotubes.[9] Virtually all of the studies whether based on single wall, double wall or multiple wall have shown that carbon nanotubes typically segregate at the grain boundaries of ceramics.[8,17–20] This may lead to grain boundaries weakening and consequently to the loss of strength and toughness of the composite.[11,18] The microstructure design based on the arrangement of carbon nanotubes at the grain boundaries and/or within the grains plays an important role in tailoring the functional and mechanical properties of the composites as observed in our earlier studies.[21,22] In addition, it allows to generate inherent thermal residual stresses in the matrix to improve its mechanical performance.[23] For instance, in traditional whisker/fiber reinforced ceramic composite, the brittle whisker that has significantly larger diameter and longer straight length as compared to flexible carbon nanotube, penetrates inside the alumina grains.[17,19] The debonding of the optimally designed interface makes the crack propagation more difficult and whisker pullout has been considered as a major contribution in the toughness improvement of the composite.[17,19] However, larger size whiskers engender larger flaw that may lead to lower strength and hardness of the composite.[17,19]

Several studies have shown that crack bridging, carbon nanotube pullout and crack deflection are the key mechanisms for toughening in ceramic/carbon nanotube composites.[9,15,16,24] Generally, the presence of nanotubes at the grain boundaries results in more likely uncoiling or stretching induced toughening due to their entanglement among adjacent ceramic grains.[17,19] However, comprehensive understanding of these mechanisms and their origin, including how they influence the mechanical properties are still lacking in alumina based multiwall carbon nanotube composites.[15] Despite the extensive work on toughening in carbon nanotube/ceramic composites, there has been almost no direct evidence on the classical pullout induced toughening by nanotubes within alumina grains.[15,25,26] In addition, no sign of resulting residual holes left by pulling out of nanotubes were reported as observed in the conventional nonflexible straight whisker/fiber reinforced ceramic composites. Therefore, the presence of carbon nanotubes typically at the grain boundaries leads to lack of resistive pullout induced toughening in ceramic composites.[15,19] This shows that the full potential of carbon nanotube reinforcement has not been utilized effectively in ceramics due to none or negligible activation of pullout induced toughening in contrast to conventional whisker/fiber reinforced ceramic composites.

Numerous advantages have been foreseen for the nanoscale flexible reinforcement of carbon nanotubes inside the alumina grains such as effective strengthening and toughening due to their flexibility, smaller size and exceptional strength. Contrary to conventional whisker/fiber reinforced alumina composite, MWCNT would not produce larger flaw, in fact, no flaw due to its nanoscale size as compared to conventional whisker/fiber. In addition, carbon nanotubes inside alumina grains are highly effective to transfer load from matrix to MWCNTs since the thermal expansion mismatch between alumina and MWCNT may provide a stress induced resistive interface with modest interfacial strength.

Therefore, in the present study, mechanical properties of alumina reinforced by MWCNTs were scrutinized. Contrary to most of the work conducted so far, this study shows that MWCNTs are residing not only at the grain boundaries, but also within the alumina grains and provide a synergistic combination of classical and novel toughening mechanisms observed in these composites. The toughness was measured by the proven direct toughness measurement, i.e. single edge notch beam method.[21] Key toughening mechanisms were scrutinized in highly disordered MWCNT/alumina composites. The activation of pullout induced toughening was identified and substantiated by in situ evidence for the first time in MWCNT/alumina composites.

2. Experimental procedure

The high purity >99.99%, agglomerate free, ultrafine, alpha-alumina powder having an average particle size of ≈0.2 μm was commercially obtained from Daimei Chemical Co. Japan. The MWCNTs were synthesized by the catalytic decomposition of propylene on Fe/Al_2O_3 catalyst, possessing an outer diameter in the range of 10–20 nm and several micrometers in length.[27,28] Although much research has been conducted for uniform mixing of CNTs in ceramics, the agglomeration of CNTs at higher vol.% may be minimized but cannot be avoided fully in the composite.[8,14] Usually acid treatment and surfactants are employed for homogenous mixing of nanotubes in ceramics. In this method carbon nanotubes are susceptible to mutilate or partial damage, leading to decrease or total loss of extraordinary strength leverage of nanostructures similar to the damage of carbon nanotubes in high temperature and longer duration sintering.[9,10] By contrast, in this work special care was taken to ensure uniform distribution of carbon nanotubes in the composites. Pristine alumina and other three compositions 1.1, 6.4 and 10.4 vol.% of MWCNT were processed as described elsewhere.[10,21] In brief, alumina was ultrasonically mixed in ethanol with simultaneous application of mechanical stirrer for half an hour. Similarly, MWCNTs were separately mixed in ethanol ultrasonically with simultaneous application of mechanical stirrer for half an hour. Later on, the two slurries were combined and homogenized ultrasonically and mechanically for another half an hour. Further, mixing was carried out by ball milling for 24 h and then the uniformly dispersed MWCNTs and alumina in ethanol were dried through rotary vaporizer. The ball milling was performed in a mild manner at a moderate speed using the zirconia ball media, which is not detrimental to carbon nanotubes.[10,29,30] The powder mixtures were