

Multi-Walled Carbon Nanotube Reinforces
Alumina Ceramic Matrix Composites by Novel
Powder Technology (粉末冶金法によるアルミナセ
ラミックス基カーボンナノチューブ分散強化型複合
材料に関する研究)

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論文内容要旨

Remarkable mechanical, electrical, thermal, optical and biomaterial characteristics of carbon nanotubes (CNTs), as well as their intrinsic chemical inertness, large aspect ratio, and high surface-to-volume values have inspired researchers to focus on composites containing CNTs with the aim of improving properties of conventional materials [1,2]. However, poor interfacial compatibility and wetting between the CNTs and the host matrix, and strong CNTs entangling caused by attractive Van der Waals forces are obstacles to achieving their intrinsic benefits to the matrix [3,4]. Thus, a great deal of attentions has been devoted to breaking up the CNTs inhomogeneous space-filling network to individually and uniformly disperse them within the matrix, and also improving the CNT surface compatibility with the host matrix with the aim of overcoming drawbacks to the processing of homogeneous composite powders specially with high CNT concentrations. Difficulties experienced to achieving homogeneous and tight CNTs dispersion within the conventional materials are found to be more pronounced for ceramics with their outstanding chemical stability preventing their homogeneous and atomic-level blending with the chemically stable CNTs. Different approaches like conventional powder processing [5], in situ nucleating CNTs or matrix [6,7], and colloidal processing [8] were proposed to overcome these obstacles, but they failed to mass-produce homogeneous CNT-ceramic matrix composite powders with high interfacial compatibility, and achieved only small improvements after consolidation. Our strategy to overcoming the issues of dispersion and interfacial compatibility, is mass-producing individually alumina-decorated CNTs with optimized and controlled compositions, and directly sparks plasma sintering (SPS).

The process of decorating individual CNTs with the alumina particles involves mildly incorporating stable suspension of the functionalized, slightly disordered CNTs to that of vigorously mixing surfactant-less alumina with the same acidic pH, and then leaving the turbulent mixture unshaken for a while, and finally collecting the individually alumina-decorated CNTs settled below a completely transparent supernatant. For specific alumina concentrations, electro-static attractive potential prevailed between the oppositely charged and well-dispersed CNTs and alumina particles at an appropriate pH can lead to their tight bonding, total sedimentation, and complete supernatant transparency indicating that no undecorated and aggregated CNTs loosely bound to the matrix are dispersed within the

homogeneous composite powders. Supernatant transparency has been proposed for the first time to determine the optimized compositions required to obtain homogeneous composite powders. Pure alumina and homogeneous composite powders have been then SPS-consolidated and characterized. This method is applicable not only for small CNT amounts, but also for a broad range of CNT concentrations. Possibility of using high-quality precursors, exact controlling the CNTs amount in the composite and mass-producing individually decorated CNTs with optimized compositions, even in high CNT concentrations are merits of this approach impossible to achieve by conventional and in-situ nucleating-based methods. Using this approach, CNTs or carbon fibres-containing composites with different matrix materials promising for a variety of applications may also be successfully fabricated, once simply attractive electro-static or electro-steric forces prevail between their modified surfaces.

Due to the difficulties experienced in removing wrapped or grafted surfactants during high-temperature sintering process or tying up of functional groups in these systems, and on the other hand, enhancement reported on the load-carrying capability of the slightly disordered and crystalline multi-walled CNTs [9,10], surfactant-less, slightly disordered, crystalline multi-walled CNTs prepared by controlled acid reflux have been employed in this work [3,4]. Crystallinity, graphitic ordering, surface functionalities, and microstructure of the pristine and well-treated CNTs have been characterized [3], approving successful preparation of the surfactant-less, hydrophilic, slightly-disordered and crystalline CNTs by controlled acid treatment. Considering supernatant transparency, the CNT concentrations required to completely attract and settle the well-dispersed alumina particles have been determined to be in the range (2.4 - 16 vol.%) in case of 150 mg alumina powders. This composition range can be affected by surface nature, attractive force, and alumina concentration. Microstructures of the composite powders containing 2.4, 3.5 and 16 vol.% CNT indicate homogeneous and tight dispersion of the individual CNTs within the alumina matrix without any aggregation [3,4]. Total wrapping or partial alumina decoration of the individual CNTs (Figure 1a) leads to the creation of the CNTs network encompassing tightly the alumina matrix; i. e., a network made of individually dispersed CNTs acts as a substrate for alumina particles to be homogeneously and tightly deposited on. This intimate bonding can provide higher density and effective load transferring from the matrix to the CNTs after consolidation.

Irreversible interfacial bonding caused by the strong electrostatic attractive potential between the negatively charged CNTs and positively charged alumina particles (~80 mV zeta potential difference [4]) has been disclosed for the first time by centrifugal consolidation of the ultrasonicated composite powders in the water, in which no segregation has been found in case of optimum compositions, which are thought to be originated from the high interfacial compatibility and wetting promising for effective load transferring and mechanical reinforcement after consolidation [4] (Figure 1a).

The considerable reinforcement has been achieved after consolidation, which experimentally shows the promising reinforcing effect of the surfactant-less, slightly disordered CNTs, as also predicted elsewhere [3,9,10]. SPS of the composite powders containing 3.5 vol.% surfactant-less, hydrophilic, slightly disordered, crystalline CNTs homogeneously dispersed within the alumina matrix has led to the about 70% increase in the fracture toughness from 3.12×10^6 for monolithic to 5.20×10^6 Pa.m^{1/2} for nanocomposite bulk with relative densities of 99.5 and 99% respectively [3,4]. Reinforcement mechanisms have been thoroughly examined in our previous papers [3,4]. The CNTs are shown to be uniformly and individually dispersed not only in the alumina grain boundaries but also inside the grains, indicating success of our novel powder processing approach to homogeneously disperse them within the nano-sized alumina powders (Figure 1a) [4]. The fracture mode is mostly intergranular. The CNTs homogeneously situated along

the propagating matrix crack are capable of bridging, and therefore, restraining further crack opening and growing. Crack is shown to deflect along the continuous CNT-matrix interface, rather than propagating through the CNTs. Crack deflection and bridging considered as toughening evidences in micron-scale fiber composites, can thus be also occurred in nano-scale CNT-alumina matrix composites, consistent with Xia et al. report [11]. The CNTs are shown to be pulled out from the matrix during crack bridging; i. e., bridging phenomenon is necessary to cause pullout of CNTs from the matrix. The work required for the CNTs removal against any interfacial frictions may contribute to effectively dissipate fracture energy and thus, major reinforcement. Interfacial compressive stresses formed during densification, may enhance these frictional forces, and therefore, the CNT reinforcing efficiency, especially in dense samples providing intimate and tight interfacial contacts. According to the high resolution transmission electron microscopy (HRTEM) images, some CNTs are observed to be homogeneously implanted inside the grains, and contribute to the ceramic's grains locking. The intimate interface and existence of no interfacial intermediate compounds or nano pores is promising for effective transfer of CNT characteristics to the matrix (Figure 1a).

A unique approach has then been proposed to directly realize crack bridging strength (Pullout nature) and elastic-plastic buckling resistance of the CNTs implanted in alumina ceramic. The CNT crack bridging strength was determined to be about 4 GPa for the employed SPS processing condition [12]. The structural irregularities of the slightly disordered multiwalled CNT implanted within the alumina matrix are the possible reason for causing such a high interfacial friction. The radial buckling of the CNTs implanted in the matrix is elastic and reversible, promising for achieving a considerable pullout friction during composite cracking. The lower stress limit for the plastic buckling of the alumina-implanted CNTs is about 25 GPa without any fracture and plastic deformation. Observation of the pullout and plastic buckling of the CNTs in the fracture surface thus proves the high amount of energy dissipation by the CNTs during fracture, thereby effectively reinforcing the composite (Figure 1b) [12].

The composite powders prepared using our recently established powder technology [4] have been also employed to fabricate CNT-based functionally graded structures (FG) with in-depth graded properties and functionalities promising for a variety of challenging structural, electronic, and biomaterial applications [13,14]. The FG concept can be successfully employed to bridge conventional ceramics to their nanocomposites containing a high concentration of CNTs, promising for unexplored yet a variety of challenging and novel applications (Figure 1c) [13,14].

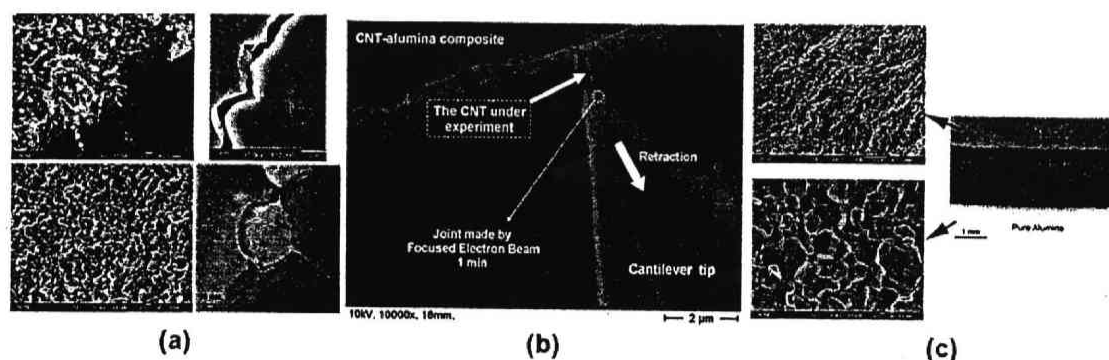


Figure 1. (a) FE-SEM and HRTEM images of the individually alumina-decorated CNTs, and fracture surface, crack profile, and intimate CNT-alumina interface of the SPS-consolidated composite; (b) The way the selected CNT and cantilever tip are manipulated. By retracting the cantilever tip along the tube axis (X-direction), a tensile load is applied to the CNT, and the work needed to pullout the CNT can be calculated from the cantilever deflection; (c) CNT-based, functionally graded alumina ceramic (An approach to bridge conventional ceramics to their nanocomposites containing a high concentration of CNTs)

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論文審査結果の要旨

飯島により 1991 年に発見されたカーボンナノチューブ(CNT)は、様々な優れた性質を有するため CNT 単相だけでなくそれを他の材料と複合化した機能性複合材料として期待されている。しかし、アスペクト比が極めて大きいナノファイバーであるため、凝集体を解し第 2 相マトリックスに均一に分散させることが難しくセラミックスや金属との複合化は依然として成功例に乏しい。本論文ではセラミックス基 CNT 複合材料に的を絞り、その作製プロセス、高機能化メカニズムの解明および高機能性材料としての可能性を明らかにすることを目的としている。まず、CNT の表面処理によって親水性を改善し、セラミックス粉末とのヘテロ凝集作用を利用してセラミックス粉末と CNT が均一に、また、高含有率で混合する方法を提案し、次にこの複合粉末を短時間で加圧焼結し、その機械的特性の評価を行い、強化メカニズムについて詳細な検討を加えたものである。

本論文は全編 6 章で構成されている。

第 1 章は序論であり、研究の背景および目的を述べている。

第 2 章では、酸処理による CNT 表面処理およびアルミナとの均一微細混合について、その方法、条件の最適化について述べている。表面処理によって CNT の親水性が改善され、PH 調整によって CNT は負、アルミナは正に帯電することから、それぞれのコロイド溶液を攪拌混合することによるヘテロ凝集作用によって CNT 表面にアルミナ微粉末が強固に付着した混合粉末を作製した。CNT の体積分率は 16vol% におよぶ従来にない成果を得ており、応用の範囲を飛躍的に高めた。一方、表面処理によってわずかに構造欠陥が導入されるが、後の章で述べるように、むしろこのことがアルミナマトリックスとの滑りを妨げるのに効果を発現する可能性を示している。

第 3 章では、均一微細に混合した CNT/アルミナ混合粉末を放電プラズマ焼結法により焼結固化し、その機械的評価を行った結果について述べている。3.5vol% CNT 複合材料の破壊じん性値はアルミナ単相材に比べて 70% 増加することを明らかにした。焼結体の相対密度はほぼ理論密度であり、CNT/アルミナ界面は反応層も無く、数 nm 程度の CNT 欠陥部においても密着しており引き抜きに対する抵抗とあることが示唆された。

第 4 章では、FE-SEM 内で CNT の引き抜き試験を世界に先駆けて実施し、アルミナマトリックスからの CNT 引き抜きの in-situ 観察、および CNT 内側の層の引抜きについても初めて観察に成功している。CNT はアルミナマトリックス内での圧縮残留応力により潰された状態になっているが、それは塑性変形ではなく弾性的に変形させられたものであることが示唆され、引抜きに対する抵抗に寄与していることが示された。

第 5 章は、傾斜機能材料 (FGM) への適用であり、アルミナ相から 16vol% CNT まで CNT 体積分率を変化させた FGM が作製できることを示し、その応用について言及している。

第 6 章は、本研究をまとめた総括である。

以上要するに本論文は、セラミックス基 CNT 複合材料に的を絞り、CNT 表面処理とヘテロ凝集作用による均一に混合された CNT/アルミナ複合粉末の作製、焼結ち密化、および FE-SEM 内での CNT の in-situ 引抜き試験と CNT/アルミナ界面の詳細な観察から強化メカニズムを検討したもので、基礎的研究ばかりでなく工学的応用についても言及しており、材料システム工学の発展に寄与することが少なくない。よって、本論文は (工学) の学位として合格と認める。