Fabrication and Characterization of Al-CNT Composites by a Combined Process of Spark Plasma Sintering and Hot Extrusion (アルミニウム/カーボンナノチューブ混合粉末のパルス通電焼結・熱間押出成形体の作製および材料特性評価に関する研究)

	コン　ハンサン
氏名	Kwon Hansang
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指導教員	東北大学教授　川崎　亮
論文審査委員	主査　東北大学教授　川崎　亮　東北大学教授　粉川　博之 東北大学教授　藤田　文夫

1. Introduction

In view of their excellent properties, carbon nanotubes (CNTs) have been the focus of researchers' interests since their discovery by Iijima in 1991 and have been labeled the "material for the 21st century."[1] CNTs are known to have excellent chemical stability, high thermal conductivity, versatile electrical characteristics, and surpassing mechanical properties that offer useful applications in various fields of industrial materials.[2] As for their structural applications, it is expected that the fabrication of metal-, ceramic-, and polymer-based CNT composites with high-strength and toughness will be possible.[3-5] In particular, CNT-Al matrix composites have the potential to be alternative ultralight materials with higher strength and ductility. Indeed, available CNT-reinforced-polymer-based composites are widely being realized by various techniques based on chemical and/or physical approaches.[6-9] On the other hand, the fabrication of metal composites reinforced by CNTs is currently falling behind as compared to polymer- and ceramic- CNT composites, due to issues such as dispersion, alignment, and interface strength. Casting approaches, which are often employed for conventional metal matrix composites, are not available for metal-CNT composites with large density differences. Although powder metallurgy techniques are appropriate, the traditional ones do not seem to allow the dispersion of bundled CNTs with strong van der Waals forces and high interfacial bonding. To overcome these problems, Cha et al. found a molecular level mixing method for CNT-Cu composites by means of a salt containing Cu ions.[10] They demonstrated that the improvement in dispersion brought a certain increase in the strength, but it was a small one, from 350 to 450 MPa with degradation in elongation of 50%. Deng et al. reported the mechanical properties of CNT-Al alloy composite materials formed by a cold isostatic press and hot extrusion.[11] Amal et al. also fabricated CNT-Al composites by a powder rolling technique.[12-14] However, such relatively traditional processes have achieved only small reinforcements due to poor dispersion and interface bonding. Thus, the prospective mechanical properties of CNT-metal matrix composites have not yet been realized, in spite of many endeavors, because of the major obstacle of homogeneous dispersion of CNT in the matrix and interfacial bonding between Al and CNT.

Here, we propose an alternative fabrication process for Al-CNT composites using spark plasma sintering (SPS) and hot extrusion from CNTs mixed Al powder prepared by a nano scale dispersion (NSD) method.[15, 16] The SPS [17-19] is employed with the aim of densifying the insinterable mixed powders by utilizing its characteristic sintering principle. Then the microstructural orientation in the sintered compact is enhanced by the hot extrusion. In the present study, we demonstrated the feasibility of high strength Al-CNT composites by means of this method.

2. Experimental Procedure

At first a precursor aimed for the dispersion of CNT in Al powder were prepared by the NSD method.[15, 16] The average diameter and length of the raw multi-walled-CNTs were 20 nm and 30 μm, respectively. The CNTs were first mixed in natural rubber (NR) with benzene solvent, and then, pure Al powder with an average diameter of 14.82 μm was added to it. The volume ratio of the CNTs and Al powder in the precursor was fixed to be 1, 5:99, 95. More details of this process can be found in our previous reports.[15, 16] The precursor was heat-treated at 500℃ for 2hrs in an argon atmosphere (1 ℓ/min. flow rate) to evaporate the NR away. The obtained Al-CNT mixture powder was sintered in a ϕ15mm carbon mold under a pressure of 50MPa using a spark plasma sintering

device (SPS-S515) made by Sumitomo Coal Mining Co. Ltd. The sintering temperature was varied from 480℃ to 600℃, and the heating rate and holding time were fixed at 40℃/min and 20min, respectively.
The sintered compacts were extruded in a 60° conical die at 400℃ with a 500kN press (UH-500kN, Shimadzu Corporation). The extrusion velocity and the extrusion ratio were fixed at 2mm/min and 20, respectively.
The microstructures of the samples after the every step were observed by a field-emission scanning electron microscopy (FE-SEM). The Raman spectroscopy served to evaluate the disorder of the CNTs after each step. For evaluation of tensile strength, the extruded bulks were machined into test pieces with a diameter of 3 mm in accordance with ICS 59.100.01. The tensile tests for three test pieces in every sintering temperature were carried out with a universal testing machine (AUTOGRAPH AG-I 50 kN, Shimadzu Co. Ltd. Japan).

3. Results and Discussion

Figure. 1 shows field-emission scanning electron microscopy (FE-SEM) micrographs of a particle in the mixture powder after the heat-treatment. The NR was perfectly removed by the heat-treatment, and the Al particles almost kept their spherical shape even through they underwent the kneading and heat treatment. Furthermore, the CNTs were uniformly and omnidirectionally dispersed onto the surfaces of every Al particles, as seen in Fig. 1 (b).

The SPSed compacts were successfully densified up to 96.1% in relative density. In general, Al powders have low sinterability because stable oxide scale on the Al particle surfaces prevents the direct contact of particles.[17-19] The achievement of high density was attributed to a certain degree of destruction of the oxide scales by the loaded pressure and especially the specific surface cleaning effect of the SPS.[17-19]

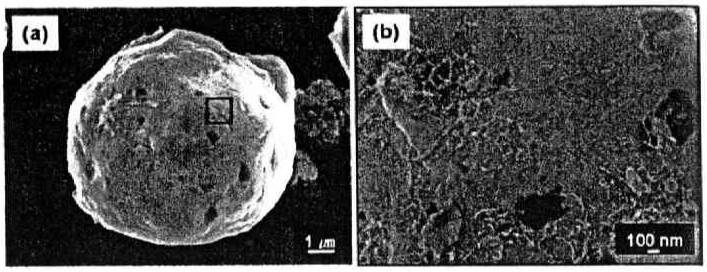

Fig. 1. Field emission-scanning electron microscope images of the Al-CNT mixed powder after the heat-treatment: (a) overview of a Al particle, and (b) higher-magnification image of the surface in (a) (the thin strings on the surface are the CNTs).

Figure 2 shows a chemically etched cross-section of the SPSed compact. The etchant used (5% sodium hydroxide solution) is able to strike only the neighborhood of the CNTs. Thus, the network of etched grooves with uniform thickness implies that all the CNTs exist uniformly in the grain boundary. The particle sizes of the matrix were almost the same as the starting Al particle size even though it was processed at the high temperature of 600℃, because the particle growth was suppressed by the rapid heating (40℃/min) and applied pressure by the SPS.

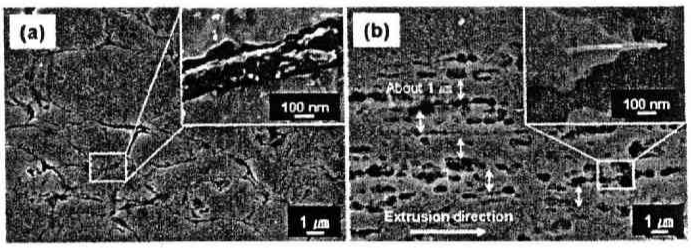

Fig. 2. Micrographs of chemically etched cross sections of Al-CNT SPSed compact and (b) extruded Al-CNT composite. The etch pits and grooves imply the existence of the CNTs. Insets in (a) and (b) show the grain boundaries.

The Raman spectroscopy served to evaluate the disorder of the CNTs after each step. Figure 3 shows the Raman spectra[20] of the raw CNTs, SPSed Al-CNT compact, and extruded bulk. The peaks at 1572.7 and around 1320 cm^{-1} correspond to a typical G-line (Graphite) and a D-line (Defect), and the relative intensity between the two peaks, I_D / I_G is known to provide information about the quality of the internal CNTs. There is no change in the value of I_D / I_G, nearly 0.8, through the SPS process. The harmful influence of heating on CNTs is often a concern, but this result conclusively verified that the SPS is an effective way to consolidate the CNTs and Al without damaging the CNTs.

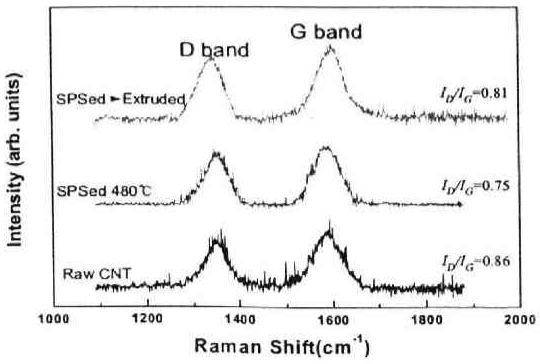

Fig. 3. Raman spectra of the raw CNT, SPSed Al-CNT compact, and extruded Al-CNT composite.

The extrusion process further elevated the density to about 98%. Figure 2 (b) shows a chemically etched cross-section of the extruded composite. The microstructure of the extruded composite was extended in parallel with the

extrusion direction, and the grain size was reduced to around 1 ㎛ in the minor axis. The CNTs in the grain boundaries were also oriented in the same direction. In addition, distinct interfacial defects between the CNTs and matrix were hardly observed (the void on the right side in the inset is an etch groove). As a result, our combinatorial method successfully produced dense Al-CNT composites with uniformly dispersed and well embedded CNTs.

Figure 4 shows the stress versus strain curve of the extruded Al-CNT composites, compared to extruded pure Al obtained with the same processes. The extruded composites exhibited a tensile strength of around 200MPa, which was 400% that of the extruded pure Al. This huge enhancement did not involve work hardening and grain refinement effects because the compared pure Al underwent the same extrusion and had the same particle size as the composites. Surprisingly, the composites maintained or exceeded the good ductility of the pure Al with an elongation of 20%. The prior researches on Al-CNT composite materials achieved less strengthening, only up to 130MPa with CNT additions of 0.5~5 vol. percent.[12, 13] In comparison with such values, the present strength achieved by the CNT addition of only 1 vol. % is impressive. Here, we also compared with the theoretical strength of fiber-reinforced composites calculated by the Kelly-Tyson equation as follows.[21]

$$\sigma_c = \sigma_{ff} V_f \left(1 - \frac{l_c}{2l}\right) + \sigma'_m \left(1 - V_f\right) \quad (1)$$

The values 30 m, 1 vol. %, and 50MPa were used for the average length of fiber l, volume fraction of fiber V_f, and strength of the matrix σ'_m, respectively, based on the experiment. l_c represents the length of the fiber when the composite material is broken. It may be said that l_c equals l. σ_{ff} represents the tensile strength of the fiber, but the exact strength of CNT is currently uncertain and unobtainable. Thus, it is meaningless to try to directly calculate the theoretical strength available for a comparison. Even so, the experimentally obtained strength values were used to inversely calculate a fiber strength of 35GPa, which well matches the reported strengths of MWCNTs, 10~60GPa.[22] The theoretical calculation is essentially based on the assumptions of the perfect dispersion, alignment, and interface bonding of CNTs. In other words, one may say that the suggested method fairly realized the ideal Al-CNT composite, able to satisfy the expected enhancement.

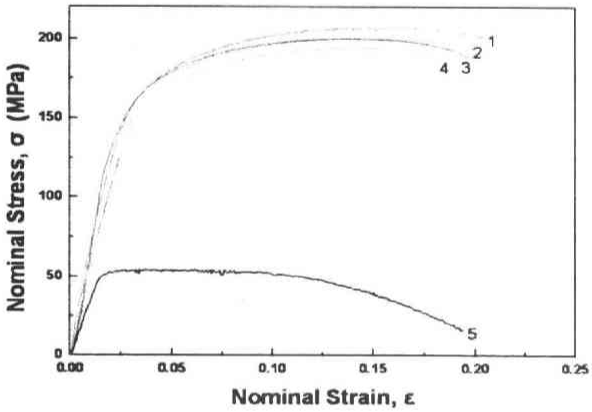

Fig. 4. Stress-strain curve of the extruded Al-CNT composites with the various SPS temperatures of 480℃ (1), 500℃ (2), 560℃ (3), and 600℃ (4), and for extruded pure Al at 600℃ (5).

The fractographies of the composite after the tensile test are shown in Fig. 5. The fracture surface had a lot of dimples associated with ductile fracture as shown in Fig. 5 (a).

The appearance of dimples means that the interfaces between the Al particles were very strongly metal-metal bonded. Furthermore, higher-magnification observation of the dimple walls found a lot of restages of bridging between the fractured Al matrices as seen in Fig. 5(b). These bridgings were obviously formed by the CNTs wrapped in the matrix, and moreover, the CNTs seem not to be pulled out but broken themselves by the applied stress. This phenomenon suggests that the CNTs were implanted in the Al matrix with an extremely strong bonding force. Such strong interfaces could allow ideal load transfers from the matrix to the CNTs [21, 23, 24] and furthermore, avoid fracture initiation of the CNTs in the final stage of fracture. As a result, the remarkable increases in strength and the maintaining of elongation became possible in parallel. In a general way, it is difficult to form substantial interfaces between Al surrounded by a strong oxide scale and chemically stable CNT. However, in this case, it is estimated that the surface cleaning

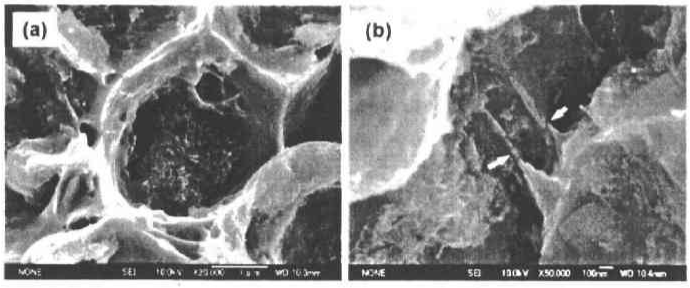

Fig. 5. The fracture surface of the extruded Al-CNT composite after tensile test. (a) Some dimples and (b) higher-magnification image of inner edge of dimple bottom. The white arrows indicate bridging and fractured CNTs.

effect of the SPS broke the oxide scale,[17-19] and the exposed Al minimally reacted to the inherent/adscititious structural defect in the outermost layer of the CNTs.[25] In addition, the extrusion pressure would enhance the bonding by mechanically thrusting the CNTs into the matrix. However, to clarify the reason why this significant enhancement of strength was obtained, future analysis from a microscopic viewpoint is needed. In any case, the combined process in this study was demonstrated to be capable of yielding the prospective reinforcing effect of CNT for pure Al. This suggests the potential to create CNT-reinforced Al alloys as a next generation ultralight material.

In conclusion, dense Al-CNT composites with homogeneous dispersion and regular orientation of the CNTs were successfully fabricated by our suggested process combining a nano-scale dispersion mixing method, spark plasma sintering, and hot extrusion. As a result, the slight addition of CNT could remarkably elevate the strength to quadruple that of pure Al while maintaining the elongation. The increase in the mechanical properties was attributed to particular strengthening by the CNTs, which strongly bonded with the matrix.

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論文審査結果の要旨

カーボンナノチューブ(CNT)は、極めて優れた物理化学的性質を有しており、その発見以来既存の材料と複合化することによって従来に無い特性を持つ機能性複合材料の作製が期待されている。しかし、ナノサイズかつアスペクト比が大きく、均一に分散した複合体とすることが極めて難しいいため依然として十分な特性が引き出された例が少ないのが現状である。本論文は特に高強度金属基ＣＮＴ複合材料に的を絞り、その作製プロセスおよび高強度化への可能性を明らかにすることを目的としている。ますナノスケールミキシングにより金属粉末とＣＮＴが均一に混合された複合粉末を作製し、次にそれを一度パルス通電加圧焼結した後に熱間押出しする金属基ＣＮＴ複合材料の作製プロセスを提案した。引張り強さは従来の報告例に比べて極めて高く、その強化メカニズムについてプロセス条件、組織および界面状態の詳細な観察から検討を加えたものである。

本論文は全編５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、熱間押出しの前に行う、ナノスケール混合法によって作製した CNT/アルミニウム混合粉末のパルス通電加圧焼結ち密化および焼結組織とその特徴について述べている。固相焼結条件にもかかわらず局所的な遷移的液相が形成されることを始めて明らかにし、この液相の形成がち密化および組織形成に重要な役割を果していることを示した。液相およびその浸透領域はアルミニウム粒子間の 200nm 程度の厚さであり、液相としての持続時間が非常に短時間と予想されるため Al_4C_3 の生成が見られるものの依然として CNT や不純物としてのアモルファスカーボンが残留した組織となる。CNT 欠陥部に形成される $A_{l4}C_3$ はアルミニウムマトリックスとの結合性がよいため荷重伝達効果を基本とする強化に有効である。したがって、定量的には難しい面もあるが Al_4C_3 の形成量や形成サイトを適度に制御することの重要性を示した。

第３章では、第２章で示した遷移的に形成される液相の量が焼結条件によってどのように変化するか調べ、Al_4C_3 の生成量など組織形成との関係を検討している。

第４章では、CNT/アルミニウム焼結体の熱間押出しによりち密な CNT/アルミニウム複合材料を作製しその機械的性質を明らかにするとともに組織との関係を基に強化メカニズムを考察している。熱間押出し材はほぼ理論密度となり、押出し方向に CNT が配向するがパルス通電焼結によるアルミニウム粒子間の特徴的組織は維持される。1vol%CNT で約 200MPa すなわち純アルミニウムの約４倍の強度が発現されることを始めて明らかにした。これは従来報告されている強度をはるかに上まわるものであり、組織の TEM 観察および破面の観察から第２章で示した CNT への局所的 AL_4C_3 の形成に起因した荷重伝達が有効に作用したためであると考察している。

５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、特に高強度金属基 CNT 複合材料に的を絞り、均一に混合された CNT/アルミニウム複合粉末のパルス通電加圧焼結と熱間押出しを組み合わせた複合プロセスの提案とその最適化、さらに高強度化へのメカニズムをプロセス条件、組織および CNT/マトリックスの界面状態から詳細に考察したものである。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。