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Synthesis, structural analysis and in situ transmission electron microscopy mechanical tests on individual aluminum matrix/boron nitride nanotube nanohybrids

Maho Yamaguchi^{a,b}, Dai-Ming Tang^{a,c}, Chunyi Zhi^a, Yoshio Bando^a, Dmitry Shtansky^d, Dmitri Golberg^{a,b,*}

^a World Premier International (WPI) Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 3050044, Japan

^b Graduate School of Pure and Applied Science, University of Tsukuba, Tennodai 1-1-1, Tsukuba 3058577, Japan ^c Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road,

Shenyang 110016, China

^d National University of Science and Technology "MISIS", Leninsky Prospect. 4, Moscow 119049, Russia

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Abstract

Boron nitride nanotube (BNNT)/aluminum matrix composite nanohybrids were fabricated through magnetron sputtering of Al onto dispersed multiwalled BNNTs with average external diameters of 40–50 nm. Aluminum phase coating tightly wrapped the BNNTs after the deposition. The coating thickness in the range of 5–200 nm was controlled by changing sputtering time. Using imaging techniques and electron diffraction analysis in a transmission electron microscope, the Al phase was found to create nanocrystalline shields around individual BNNTs. The chemical states of the hybrid nanomaterials during the initial stages of sputtering were analyzed by X-ray photoelectron spectroscopy. Direct in situ bending and tensile tests on individual BNNT–Al nanocomposites were carried out by using a dedicated transmission electron microscope-atomic force microscope holder. In parallel, high-resolution TEM images and video recordings were taken for the analysis of deformation kinetics and fracture mechanisms. The nanohybrids with a suitably thick aluminum coating (~40 nm) withstood at least nine times higher stresses compared to a pure non-armed Al metal. This pioneering work opens up a prospective pathway for making ultralight and superstrong "dream" structural materials for future automotive and aerospace applications.

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1. Introduction

Among all structural metals, low density, lightweight aluminum and its alloys are one of the most important constituents of functional components used in automotive and

* Corresponding author at: World Premier International (WPI) Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 3050044, Japan.

E-mail address: golberg.dmitri@nims.go.jp (D. Golberg).

aerospace applications. Their light weight is the key for economic usage of fuel, saving energy and decreasing environmental pollution. However, such materials are relatively soft. For example, pure Al has a very modest values of Young's modulus and ultimate tensile strength, ~70 GPa and ~40 MPa [1], respectively. These further decrease several times under heating to moderate temperatures of only 200–300 °C. Making Al tougher and stiffer would lead to significantly minimized demands for structural component sizes and their thicknesses, and in turn further reduce the overall construction weight.

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Conventional multiwalled nanotubes made of carbon (CNTs) [2] possess a Young's modulus of up to 1 TPa, which rivals that of diamond [3], and a strength of the order of 100 GPa [4–8], thus \sim 100 times of that of a typical steel, while being just one-fifth of its weight [9]. Thus, at present, the nanotubes are likely the strongest one-dimensional reinforcing fibers known to mankind. And, not surprisingly, very recently, nanotube-reinforced metal matrix composites have received increased attention from materials scientists and engineers [10]. However, the applications of the most abundant multiwalled CNTs grown from a vapor phase (through a so-called chemical vapor deposition (CVD) process) for metal matrix composites have evidenced severe fundamental problems due to CNT specific and unfavorable morphologies. That is, due to weakly bonded individual multishells, the standard CNTs are normally curled and waved, and form numerous buckles and entangled ensembles [9]. This kills the possibilities for their homogeneous distribution in a given matrix, creates macrovoids in the composite sheets, fibers and stripes which, in turn, serve as stress concentrators, and weaken matrixreinforcing fiber interface, and, in the end, lead to a material catastrophic brittle failure.

However, there is another nanotube in nature that is structurally very similar to CNTs, but functionally very different – such nanotube is made of a layered boron nitride (BN). Boron nitride nanotube (BNNT) [11] – is an amazing material whose rich potential has yet been properly and fully understood. It is extremely thermally stable, chemically inert, and does not dissolve in acids and molten salts. Whereas CVD C nanotubes start to completely disintegrate at only ~500 °C in air via oxidation, BNNTs withstand temperatures in excess of 900 °C without any traces of structural degradation or chemical modification [11].

Over the past years the present authors performed the first ever direct bending [12] and nanotensile tests [13] on multiwalled BN tubes inside a transmission electron microscope and realized that, similarly to C nanotubes, they possess a huge Young's modulus of \sim 1 TPa and an ultimate tensile strength exceeding 30 GPa. Thanks to a specific ionic-type B–N chemical bonding in multiwalled BN nanotubes and resultant strong intra-layer coupling (so-called "lip-lip" interactions), such tubes crystallize in peculiar straight needle-like morphologies (as opposed to commonly bundled and buckled standard CVD C nanotubes). Due to this feature such tubes possess characteristic multishell breakage that allow them to carry a load several times exceeding that natural for multiwalled C nanotubes at the same loading conditions [13].

Intuitively, needle-like shapes of BN tubes look remarkably preferable for their perfect distribution and even texturing/networking in any given matrix, including metals. In fact, this BN tube advantage was experimentally verified by us over the last years in respect of BN nanotube–polymeric composites [14] and BN nanotube–ceramic matrix composites [15]. The strength, toughness, elasticity and thermal conductivity of polymers and engineering ceramics have dramatically been enhanced, up to 200-300%, by adding marginal amounts of multi-walled BN tubes (only few wt.%).

We also measured the true density of BN nanotubes as only $\sim 1.4 \text{ g cm}^{-3}$ [16]. Therefore, a possible increase of strength and elasticity of an Al matrix by such low density, ultralight, but superstrong reinforcing fibers would allow one to dramatically reduce the carrying-load component dimensions and further dramatically reduce the overall structure weight, decrease fuel consumption, save energy, and reduce pollution effects if such new hybrid material may be utilized for the new generation of automobiles, aircrafts and/or spacecrafts.

However, to date BN nanotube-metal matrix composites have been given very little attention due to difficulties involved in BNNT high yield fabrication (needed for a realistic metal composite research) compared with the relative ease in making standard CVD C nanotubes. It is only during the last few years that our group at NIMS has achieved technologically meaningful amounts of multi-walled BNNTs [11]. Thus, the expected high-quality BN nanotube-reinforced metal matrix composite studies have just become feasible and timely.

Therefore, the ultimate target of the present work is the design, development and fabrication of a new prototype "dream" structural material which would be ultralight (density of only 2.5 g cm⁻³ or less), superelastic and superstrong (tensile strength in the GPa range). We are predicting that such a material should be based on a composite hybrid between an Al-based matrix and reinforcing superstrong, ultralight fibers made of straight needle-like multiwalled BN nanotubes.

In order to elucidate the regarded working principle of the proposed reinforcement approach, in this paper we for the first time fabricated, bent and tensioned the individual BN nanotube-reinforced aluminum-based nanohybrids in a transmission electron microscope equipped with an atomic-force microscopy (AFM) sensor.

2. Experimental methods

Pure "snow-white" multi-walled BNNTs were synthesized at a high yield through the so-called boron oxideassisted CVD (BOCVD) method, as was reported in our previous publications [11–14]. After subsequent purification, the nanotubes were dispersed in ethanol. Their average external diameter was \sim 40–50 nm.

BNNT/Al nanocomposites were fabricated at room temperature using magnetron sputtering (CFS-4EP-LL, Shibaura Mechatronics Corp.) of pure Al onto dispersed BN multiwalled nanotubes. Depending on the experimental requirements the tubes were placed on either a Si wafer, a Cu grid or a gold microwire (250 μ m in diameter) sharp tip. Argon was introduced as a sputtering gas at a flow rate of 20 sccm. The total gas pressure was 0.5 Pa. Aluminum (99.99%) target (75 mm in diameter) was connected to a DC power supply. The power was set at 200 W. A distance

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between the target and the substrate with dispersed nanotubes was fixed at 110 mm. The base pressure was less than 5.0×10^{-4} Pa. Before the deposition, the "pre-sputtering" was carried out for 3 min to establish the steady state of the target surface. The thickness of the sputtered Al was controlled by changing the sputtering time. The range of targeting nominal Al coating thicknesses varied from 5 nm to 300 nm.

The phase composition and crystal structures of the prepared nanohybrids were analyzed by X-ray diffraction (XRD) (RINT2000 AltimaIII, Rigaku) using Cu $K_{\alpha 1}$ radiation. Also, the morphologies, micro- and atomic structures of the nanocomposites were studied by scanning electron microscopy (SEM) (S4800, Hitachi) and transmission electron microscopy (TEM) (JEM-3000F, JEOL and JEM-3100FEF (Omega filter) microscopes). To prepare TEM samples, Al was sputtered directly on a carboncoated 3 mm Cu TEM grid with dispersed BNNTs on it. The sputtering direction was adjusted to be perpendicular to the grid plane. Energy dispersive X-ray spectrometry under SEM and TEM (EDX) (EMAX EX-220, Horiba, and JEM-3100FEF microscopes, respectively) at accelerating voltages of 10 kV (SEM) and 300 kV (TEM) was employed to identify the nanocomposite chemistry and to spatially map the constituting species.

Chemical states of the nanohybrids after the initial sputtering stages were analyzed by X-ray photoelectron spectroscopy (XPS) (Theta Probe, Thermo Fisher Scientific). All the spectra data were identified by the NIST X-ray photoelectron spectroscopy database.

Direct in situ bending and tensile tests on individual nanocomposite samples were carried out at room temperature by using an integrated AFM holder (Nanofactory Instruments) inside the TEM (300 kV JEM-3100 FEF, JEOL equipped with a $2 \text{ K} \times 2 \text{ K}$ CCD camera for imaging) [12,13,17–19]. Video recording of the deformation cycles was performed using conventional film grabber software. To construct a deformation set-up, firstly, multiwalled BN nanotubes were placed onto the edge of a gold microwire and scratching the wire over the prepared BNNT powder debris. Then, the tip with physically adhered several BNNTs was coated with Al through magnetron sputtering. It was then inserted into the movable part of the TEM-AFM holder. Calibration of the AFM cantilever and aligning processes of the individual nanocomposites were carried out before all bending and tensile tests. The spring constant of the AFM cantilever was measured to be 6.9 N m⁻¹ by pushing a blank Au tip against the cantilever and recording the force-displacement curve. Then the height of the chosen nanohybrid was adjusted to the AFM cantilever based on the focusing conditions and utilizing a standard wobber TEM function. The orientation of the nanocomposite sample was set to be nearly perpendicular to the cantilever by three-dimensional piezo-controlled movements of the gold tip with placed Al-BNNT nanohybrids at a precision better than 1 nm. For reliable clamping of the sample to the gold tip and AFM cantilever during the nanomechanical tests, two tiny candle wax droplets were placed $\sim 2 \text{ mm}$ away from the tip and cantilever ends, and the electron beam was focused onto the sample/tip and sample/cantilever interfaces for a few minutes to induce electron-beam-induced (EBID) amorphous carbon deposition. By choosing suitable electron beam conditions, the clamps were highly localized close to the nanocomposite ends, while their surface remained free of carbon contamination. Thus rigid clamping between the densely Al-coated BN nanotube sample and the Si cantilever, and the gold wire was achieved. The experimental setup for making the amorphous C clamps and performing direct bending and tensile tests is illustrated in Fig. 1. The insets in Fig. 1 show the corresponding high resolution TEM (HRTEM) images of the sample/amorphous C clamp interfaces at the two ends of a nanohybrid. The nanocomposite was bent or stretched under corresponding delicate forward or backward movements of the gold wire placed on the piezo-motor driven unit of the holder. During the sample tension, the tensile forces and real time videos were recorded in parallel, and the tensile stresses and elongations were subsequently calculated. Parallel HRTEM images were also taken for the exact measurements of the nanocomposite cross-sections and analysis of the deformation kinetics and fracture mechanisms.

During the tensile tests, the relative Z-position of a composite hybrid inside TEM, relative to the cantilever's



Fig. 1. Experimental setup for in situ TEM bending and tensile tests on individual BNNT/Al composite nanohybrids; the insets show HRTEM images of a nanocomposite sample in the vicinity of amorphous C clamps created by using electron-beam-induced deposition (EBID). The structural details of interest discussed within the text are marked.

height, was maintained by continuous focusing conditions monitoring. However, it was still practically difficult to ensure that the sample was exactly aligned with the cantilever. Therefore, the length, displacement and elongation of the nanocomposites were calculated by considering the angle between the tested nanohybrid and the deflection direction of the cantilever, and the height difference. And the stress was calculated as: $\sigma = \frac{\cos \theta}{S}$, where S is the crosssectional area of the sample, k is the spring constant, Δx is the deflection of the cantilever and θ is the angle between the specimen axis and the direction of the cantilever deflection.

3. Results and discussions

3.1. Structural and chemical characterizations of composite BNNT–Al nanohybrids

The synthesized BNNT-Al nanocomposites entirely preserved a one-dimensional straight morphology peculiar to the starting multiwalled BNNT templates. The thickness of the Al coating became larger in proportion to increased sputtering time. X-ray diffraction patterns of the BNNT-Al nanocomposites with decently thick ($\sim 200 \text{ nm}$) Al coatings revealed the clear peaks which were identified to a hexagonal BN (002) plane (ICSD #: 027987), and Al (111), Al (200) and Al (220) reflections (ICSD #: 044321). Other intense visible peaks were from a sample holder or a substrate. This implies that the BN phase remained untainted, and no new B- and/or N-containing Al compounds, such as AlN or AlB₂, formed during sputtering. Some reports have shown similar results [20-23], but in some others new peaks peculiar to boride or nitride compounds were noticed. However, in the latter cases the contents of BN nanotubes were quite low [24], or the samples were bulky [25,26], or they had undergone prolonged heat treatments.

In order to further confirm the presence of the desired Al coatings on BNNTs, detailed SEM and TEM observations were conducted. SEM images, shown in Fig. 2, demonstrate that sputtered Al thickness is indeed coincident with the expected sputtering rate. The nominal Al layer thickness (as was set for a magnetron sputter) varied from 5 nm to 300 nm. Fig. 3 displays the EDX analysis data obtained from a representative BNNT-Al sample coated with a 200 nm Al layer (Fig. 3a). Although the light elements (B and N) region is not well resolved (inset in Fig. 3a), a clear and strong Al peak is apparent. Traces of oxygen are also visible. Fig. 3b shows spatial distribution of Al within the sample. The Al intensity is clearly seen on all one-dimensional morphologies, thus confirming a uniform metal coating on all dispersed BNNTs. Fig. 4 depicts representative TEM and HRTEM images of individual BNNT-Al nanocomposites of various thicknesses together with selected area electron diffraction (SAED) patterns. It is again obvious that the coating thickness increases with increasing sputtering time. Also it is apparent that the coatings appear to be polycrystalline for all thicknesses studied. As particularly seen in Fig. 4a and b, multiwalled BN nanotube cores remain undamaged under the coated Al shield. The DP reflections come from the core BNNT arms and surrounding Al nanocrystals (as marked in the insets to Fig. 4a, c, and e). It is noted that during sample tilting in TEM (up to $\pm 20^{\circ}$ in X-Y directions, Fig. S1, Supplementary data) its appearance does not change, implying uniform Al coatings over the entire tube surface (Fig. S1). Thus the sputtered Al phase has uniformly wrapped the BN nanotube cores.

XPS was used for the elemental analysis of B, N, O and Al states to determine the chemical bonding nature during the initial stages of sputtering. Fig. S2 (Supplementary data) displays a survey XPS spectrum of a BNNT–Al 20 nm nanocomposite on a Si wafer. In terms of binding energies, the peaks at ~73 eV, 191 eV, 398 eV and 532 eV correspond to the Al2p, B1s, N1s and O1s, respectively. Fig. 5 shows enlarged XPS spectra of Al2p, B1s, N1s and O1s on the sample surface. There are two peaks of Al (Fig. 5a). One weaker peak at 71.9 eV indicates metallic Al and the other main peak at 74.8 eV is peculiar to Al₂O₃. The described XPS results imply three major conclusions: (i) Al coating may be oxidized during sputtering (e.g. this explains a minor O peak for the EDX spectrum in Fig. 3); (ii) multiwalled BN nanotube cores entirely with-



Fig. 2. (a-h) Representative SEM images of BNNT-Al nanocomposites with various nominal thicknesses of Al coatings (as set for a magnetron sputter). The coating thickness proportionally increases with increasing sputtering time.





Fig. 3. (a) SEM image of a representative BNNT–Al nanohybrid with a 200 nm Al layer; and (b) its EDX Al K_{α} mapping. The inset in (a) shows a recorded EDX spectrum displaying strong Al and weak O peaks coming from the coating, and weak B, N peaks originating from the core multi-walled BN nanotube. (X axis: keV; and Y axis: counts (arbitrary units))

stand the magnetron sputtering without losing integrity of B-N bonds and straight morphology of well-structured shells; (iii) no intermediate and interfacial boride or nitride phases, e.g. AlB₂ or AlN, have been formed between the BN tube cores and Al coats during sputtering in line with the XRD data discussed above.

The described facts conclusively show that magnetron sputtering at room temperature, being a relatively simple and straightforward procedure, is fully able to produce desired Al–BNNT nanocomposites with various thicknesses of Al phase shields. Compared to other methods of making nanotube–metal composites, e.g. powder metallurgy, it does not require a multi-step procedure involving high pressures and/or high temperature treatments [10,24]. Fabricating metal–BNNT nanocomposites was also reported during BNNT synthesis by chemical vapor deposition (CVD) using a metal catalyst [11]. However, in the latter case it was impossible to control the desired amount of metal within a composite. It is emphasized that, to date, there have been only two reports pertaining to metal (i.e. gold [27], nickel, titanium and aluminum [28]) coatings on BN nanotubes. Chen et al. [27] used sputtering to improve the field-emission properties, whereas Obrastsova et al. [28] used a destructive ion-implantation method for to coat nanotubes and/or fill them with metals. The data acquired in our present work show that the regarded magnetron sputtering procedure is an effective tool for the realization of multiple merits of BN nanotubes and their metal composites in various branches of technologies such as electronics, mechanics, etc.

3.2. Mechanical properties of individual BNNT-Al composite nanohybrids

At first, bending tests were carried out for an individual BNNT/Al nanocomposite covered with a 40 nm layer of Al. The data are presented in Fig. 6. Initially, the nanohybrid had a straight morphology inheriting this shape from a starting BNNT template (Fig. 6a). Under bending, it turned into an "S" shape with a bending strain concentrated at the middle and close to the clamp portions, respectively (Fig. 6b-d). After that, the nanocomposite fractured at a maximum bending angle of $\sim 50^{\circ}$ (Fig. 6e). The failure started within the Al shield, whereas the nanotube core initially survived; it broke only at the final stage of bending. In order to get deeper insights into the deformation kinetics, detailed microanalysis of this experimental run using TEM is illustrated in Fig. 7. The starting status of the Al-100 nm-BNNT nanohybrid is depicted in Fig. 7a-c at different magnifications. An ultimately straight BNNT core is surrounded by a thick Al shield with numerous Al nanoparticles seen (Fig. 7b and c). After bending and breakage of the nanocomposite (Fig. 7d) the broken BN core was partly pulled out of the Al shield (Fig. 7e). The failure of the core took place in a characteristic "sword-in-sheath" fashion peculiar to inorganic nanotubes [29]. Overall, under bending the BNNT/Al nanocomposite revealed decent toughness. The crack initiated on the tensed side of the sample and did not propagate through the entire nanocomposite directly and immediately. It was likely deflected by numerous Al nanoparticles and probably followed the path of the particle boundaries network, thus facilitating the effective dissipation of strain.

Under tension (Fig. 8a), an individual BNNT/Al nanocomposite covered with a 40 nm layer of Al elongated uniformly, showing clear strain contrasts within the Al phase, indicative of strong interfacial bonding and an effective stress transfer at the nanotube/metal composite interface. Until the mechanical limit of our measurement setup (~ 6000 nN), the BNNT/Al nanocomposite responded purely elastically to the tensile force, as shown in Fig. 8b, withstanding the tensile stress of at least 0.36 GPa. It is noted that we had to terminate the stretching experiment due to reaching the MEMS sensor force limit; thus, the present nanohybrid is definitely stronger than that figure. To compare: the ultimate tensile strength of a typical metallic Al has been known to be only ~ 40 MPa. Thus





Fig. 4. (a, c, e) Low-magnification TEM images; and (b, d, f) high-resolution TEM images showing various nanohybrids and the interfaces between Al phase and the multilayered BNNT external walls of a BNNT–Al nanocomposite. (a, b) a nanohybrid with a 20 nm Al layer thickness. (c, d) a nanohybrid with a 30 nm Al layer thickness; (e, f) a nanohybrid with 200 nm Al layer thickness; excellent crystallinity of the BN walls is clearly preserved on all images. The insets show indexed selected area electron diffraction (SAED) patterns, characteristic of polycrystalline Al coatings on well-structured BN nanotubes.

the present BNNT–Al nanohybrids can indeed be dramatically strengthened with respect to a non-armed pure Al metal, revealing a striking, approximately nine times enhancement of the tensile strength.

An interfacial stress transfer and deformation mechanisms are very important for understanding recently discovered behaviors of the fabricated composites. Because of the entire electron scattering overlapping from Al crystals and BNNT shells on TEM images (i.e. the interface could not be clearly viewed edge-on without coming signals from the front and back portions of the Al shields along the electron beam direction) it is difficult to observe the Al–BNNT interface under clear atomic resolution. We prepared the cross-sectional TEM sample of a composite by using a focused ion beam (FIB) technique; however, BNNTs were destroyed by high energy ion beams, leaving only Al crystals behind. It is particularly noted that no plastic deformation was observed in our experiments and the samples were fractured within the elastic range. We thus attempted to calculate the stresses within the BNNT cores (σ_{BN}) and Al coatings (σ_{Al}) using the following formula:



Fig. 5. XPS spectra (Al 2p, B 1s, N 1s and O 1s) of a BNNT-Al hanohybrid with a 20 nm Al layer thickness. The Al spectra in (a) indicate metallic Al (73 eV) and Al in Al oxide (74.8 eV); (b, c) B-N bonded phase; and (d) oxygen in Al oxide.



Fig. 6. Representative direct in situ TEM bending test on an individual BNNT-Al nanocomposite coated with a 40 nm Al layer. (a–e) Consecutive TEM images of the bending process; scale bars indicate 1 μ m. (f) Enlarged HRTEM image of the fractured portion. The multiwalled BN nanotube core becomes visible at this portion.

$$\sigma_{BN,Al} = \frac{F \times E_{BN,Al}}{S_{BN}E_{BN} + S_{Al}E_{Al}}$$

in line with the elastic theory, where F is a force, E_{AI} and E_{BN} are the Young's modulus of bulk Al and in-plane elastic modulus of a hexagonal BN phase, respectively, and S_{AI} and S_{BN} are the corresponding cross-sectional areas of the

two phases in a given composite. The stresses in BNNT domain and Al coating for a representative BNNT/Al 20 nm sample were calculated to be 3.52 GPa and 0.24 GPa, respectively. In addition, during all the mechanical tests, the TEM contrast due to stresses was solely observed within the Al crystals. Neither dislocations nor Al crystal relo-

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Fig. 7. Structural details related to the bending experiment of Fig. 6. (a–c) Characteristic TEM images of an Al–BNNT nanocomposite coated with a 40 nm Al layer before bending and clamping at various magnifications. (d–f) TEM images of a broken nanohybrid after the bending test at various magnifications. See text for details.



Fig. 8. Representative direct in situ TEM tensile test on an individual BNNT–Al nanohybrid coated with a 40 nm thick Al layer. (a) Consecutive TEM images displaying the elongation process in time. (b) A plot of measured force against the cantilever displacement. The reached tensile strength was calculated to be at least ~ 0.36 GPa (tensile loading was terminated at a ~ 600 nm displacement due to reaching the force limit of the experimental setup). A change in the servation appearance on the plot in (b) was caused by an abrupt increase in the deformation rate at a displacement of 370 nm.

cations were found under tension. Sometimes the inner tubular shells of the BN core may even be pulled out of the outer BN layers rigidly fixed to the Al shield, as discussed later. By taking into account the accurately measured in TEM displacement difference for the initial and final stages, a total strain in Fig. 8 was calculated as 2.1%. The displacement was measured by choosing two reference positions on



Fig. 9. TEM and HRTEM images of fractured BNNT/Al nanocomposites: (a–c) a thin BNNT nanocomposite coated with 20 nm of Al, fractured in tension; HRTEM image in (b) corresponds to the remaining joint between Al coating and BNNT core on the left-hand side of the image in (a); HRTEM image in (c) corresponds to the fractured nanocomposite right-hand end in (a); note that the remaining external BN layers within the Al shield are apparent; note that the experimentally measured ultimate tensile strength of this sample was 1.47 GPa; and (d–f) a thick BNNT nanohybrid coated with 200 nm Al broken under bending; HRTEM image corresponds to the lower broken end of the hybrid in (e).

the composite sample and measuring the distance difference between them while taking into account the TEM image changes in both vertical and horizontal directions on the imaging plane under loading. We also attempted to measure the strains by in situ measuring the changes of the SAED patterns (compared to the undeformed state) during and after the tensile tests. For example, for a BNNT-Al 20 nm sample the measured d spacing for (111) Al reflection was 0.245, 0.245 and 0.231 nm, before, under and after the tensile deformation, respectively (note that 0.233 nm is the standard value for the bulk Al); also the ratio of the vertical and horizontal length of electron diffraction (ED) of the Al (111) ring was 1.04, 1.05 and 1.05 correspondingly, so that the assumed elongation may be counted to be \sim 5%, which is in the range of the standard error of electron diffraction techniques. That is the reason why we were not able to use ED data to accurately measure displacements and/or real strains.

Regretfully, at the present stage of the in situ TEM holder developments it is not possible to break and/or even provide enough stress to the thicker Al–BNNT nanocomposites (\sim 100–200 nm coatings) fabricated in the frame of this work. Indeed, the thickness of Al coatings should have an important influence on the mechanical properties and fracture behaviors of the nanohybrids. However, we still try to carefully carry out numerous tensile experiments on the samples with different Al coating thicknesses. We have accomplished the direct in situ TEM tensile tests on Al coated samples with nominal Al thicknesses of 20, 60

100 and 300 nm, see Fig. 2 (these correspond to the actual metal layer thicknesses of 20, 30, 40 and 200 nm, as accurately measured by HRTEM). As a result, we should admit that experimentally it was not possible to numerically compare the mechanical properties: the thicker nanohybrid samples could not be fractured or even sufficiently loaded during a tensile test due to the experimental force limit of the Nanofactory AFM holder. In fact, a previous paper from our group reported that most of the pure BNNT samples with a diameter of more than ~ 48 nm were not broken, and so it was difficult to obtain accurate values of the ultimate tensile strength or Young's modulus data using the present in situ AFM-TEM technique [13]. Anyway, according to the studied BNNT-Al samples which could be broken, it became clear that there is a certain difference for the fracture mechanism between thinner Al-layered and thicker Al-layered BNNT composites (Fig. 9a-f). On the one hand, when a BNNT/Al 20 nm nanocomposite was completely fractured in tension, the inner portion of BNNT shells slipped out of the outer BN layers which had remained rigidly fixed to the Al shield, as shown in Fig. 9a and b. On the other hand, a BNNT-Al nanohybrid with a 200 nm Al layer, that did not fail under tension, was managed to be cracked under bending along the Al grain boundary, as shown in Fig. 9d–f. The thinner sample fractured abruptly in a brittle way, while the thicker sample fracture (started within the Al grains) was stopped by the BNNT core and, providing the huge strength of BNNT multilayers themselves, up to 30 GPa [13]; such nanocom-

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posites may be expected to withhold greater forces and stresses.

It is worth noting that similarly positive and radical effects of multiwalled BN nanotubes on Al compressive properties have so far been noticed in a single publication dealing with these novel materials, i.e. under compression of BNNT–Al nanocomposites produced by standard powder metallurgy. In fact, a five times increase in microhardness and a three times increase in compressive strength were evidenced for Al–BNNT macrocomposites with 1.5 wt.% of BNNT fraction compared to pure aluminum [24]. These encouraging results, together with the presently carried out first ever direct bending and tensile tests of Al–BNNT composite nanohybrids, open up a wide horizon for future developments with regard to these unique "dream" structural materials of the future.

4. Conclusions

We fabricated BNNT–Al composite nanohybrids with a varying Al coating thickness, from 5 nm to 200 nm, by magnetron sputtering. XRD, SEM, TEM, XPS and in situ TEM bending and tensile tests on individual nanohybrids shed a new light on their micro- and atomic structures, chemical status and mechanical properties. We demonstrated that the applied synthetic route is an effective method for fabricating novel ultralight, superstrong BNNT–Al hybrid nanomaterials. Nanocrystalline Al coatings were documented on Al-wrapped BNNTs. The fabricated nanohybrids with suitably thick (\sim 40 nm) Al coatings on BN nanotubes (of \sim 40–50 nm external diameter) demonstrated at least an approximate nine times increase in tensile stress which they can withstand without failure, compared to a pure non-armed Al metal.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.actamat.2012.07.066.

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