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(71) Applicant (for all designated States except US): **THE GOVERNORS OF THE UNIVERSITY OF ALBERTA** [CA/CA]; Suite 400, 8308-1114, Edmonton, Alberta, T6G 2E1 (CA).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **SALIMI, Sahar** [IR/CA]; 11020 53 Avenue, #2007, Edmonton, Alberta, T6H 0S4 (CA). **GERLICH, Adrian, P.** [CA/CA]; 218 Bancroft Close, Edmonton, AB T5T 6B5 (CA).

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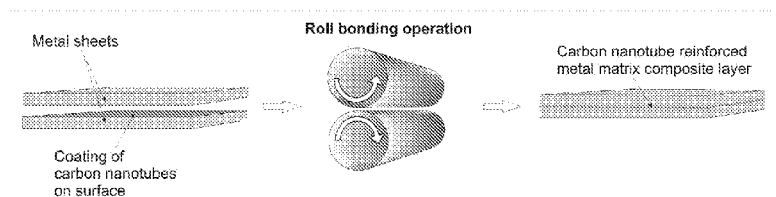


FIG. 1

(57) Abstract: Described herein are composites reinforced with nanostructures and methods for making the same. In one aspect, the reinforced composites are made by (a) applying nanostructures to a surface of a first article; (b) applying a second article to the surface of the first article comprising the nanostructures; and (c) pressure bonding the first article and second article to produce the reinforced composite, wherein the reinforced composite is not subsequently annealed after step (c). Applications of the reinforced composites are also described as well.

REINFORCED COMPOSITES AND METHODS OF MAKING AND USING THEREOF

5 CROSS REFERENCE TO RELATED APPLICATION

This application claims priority upon U.S. provisional application Serial No. 61/182,359, filed May 29, 2009. This application is hereby incorporated by reference in its entirety for all of its teachings.

BACKGROUND

10 New reinforced composites are constantly being engineered in search of stronger and lighter prototypes. Protocols and materials for making these reinforced composites are highly specialized, expensive, and time consuming. For instance, reinforced composites utilizing carbon nanotubes are known; however, the techniques used to create composites reinforced with carbon nanotubes (CNTs) are very time consuming,
15 prohibitively expensive, and often produce composites with damaged carbon nanotubes, in which the composites are not necessarily stronger due to the aggregation of carbon nanotubes. For example, these materials are often subjected to ball milling, sintering, or electrodeposition. These methods require high skill level, specialized equipment, and complex processing steps to fabricate reinforced composites. Therefore, it is generally
20 difficult to quickly, efficiently, and cost-effectively produce such reinforced composites with currently known methods.

SUMMARY

Described herein are composites reinforced with nanostructures and methods for making the same. In one aspect, the reinforced composites are made by (a) applying
25 nanostructures to a surface of a first article; (b) applying a second article to the surface of the first article comprising the nanostructures; and (c) pressure bonding the first article and second article to produce the reinforced composite, wherein the reinforced composite is not subsequently annealed after step (c). Applications of the reinforced composites are also described as well. The advantages of the invention will be set forth in part in the
30 description which follows, and in part will be obvious from the description, or may be learned by practice of the aspects described below. The advantages described below will

be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive.

5 **BRIEF DESCRIPTION OF THE DRAWINGS**

The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate several aspects described below.

Figure 1 shows a schematic of an exemplary method of fabricating the metal composite by roll bonding.

10 Figure 2 shows a transmission electron microscopy (TEM) image of a roll bonded metal (aluminum) composite after 4 rolling passes reinforced with a single layer of carbon nanotubes before the first rolling pass

Figure 3 shows a selected area electron diffraction pattern of a bright field image of a metal composite where rings correspond to the carbon nanotube material, and spots
15 correspond with crystalline aluminum.

Figure 4 shows the distribution of carbon nanotube diameters in the as-received material, and roll-bonded aluminum metal matrix composite. The number of samples measured was 110 and 117 for the as-received and roll-bonded CNT populations respectively.

20 Figure 5 shows the TEM micrograph of the as-received multiwalled CNT material.

Figure 6 shows the TEM micrograph of (a) the roll-bonded CNT reinforced aluminum composite layer with selected area diffraction pattern when viewed along the normal direction of the sheet (ND), and (b) the individual CNTs in the matrix.

25 Figure 7 shows the TEM micrograph of the cross section of the roll-bonded CNT reinforced aluminum composite material after 4 passes.

Figure 8 shows the SEM images of the interface of the roll-bonded composite sheets after they were mechanically delaminated.

Figure 9 shows the SEM image of (a) the cross section of the reinforced layer in the roll-bonded CNT reinforced aluminum composite material following etching with HF, and (b) a single CNT embedded in the aluminum.

Figure 10 shows the diameter and wall thickness measurements for the CNT base material.

Figure 11 shows (a) TEM micrograph of the roll-bonded composite with the end of a broken CNT at A, and (b) EDX spectrum of the sample at point A.

DETAILED DESCRIPTION OF THE INVENTION

Before the present articles, compositions, and/or methods are disclosed and described, it is to be understood that the aspects described below are not limited to specific compounds, synthetic methods, or uses as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting.

In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings:

It must be noted that, as used in the specification and the appended claims, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a metal alloy” includes mixtures of two or more metal alloys, and the like.

“Optional” or “optionally” means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event or circumstance occurs and instances where it does not. For example, the phrase “optionally heating” means that the metal articles and composites may or may not be heated during the methods described herein.

A weight percent of a component, unless specifically stated to the contrary, is based on the total weight of the formulation or composition in which the component is included.

Described herein are reinforced composites and methods for making the same thereof. In one aspect, the reinforced composites are made by (a) applying

nanostructures to a surface of a first article; (b) applying a second article to the surface of the first article comprising the nanostructures; and (c) pressure bonding the first article and second article to produce the reinforced composite, wherein the reinforced composite is not subsequently annealed after step (c). Each component and step in the process is discussed in detail below.

The process described herein utilizes nanostructures to produce reinforced composites possessing several desirable properties. Nanostructures can include, for example, nanotubes, nanowires, nanorods, nanoparticles, or a combination thereof. In the case of nanotubes, nanowires, and nanorods, one of the dimensions of the nanostructure is less than 100 nm. Not wishing to be bound by theory, the nanotubes, nanowires, and nanorods can align in a particular direction, which can impart unique features to the final reinforced composite. For example, nanotubes can align with their axial direction parallel to the rolling direction when roll bonding is used to make the reinforced composite. This can be very useful in controlling the properties of the reinforced composite.

The nanostructures useful herein can be composed of organic and/or inorganic materials. In one aspect, the nanostructures can be composed of organic materials like carbon or inorganic materials including, but not limited to, boron, molybdenum, tungsten, silicon, titanium, copper, bismuth, tungsten carbide, aluminum oxide, titanium dioxide, molybdenum disulphide, silicon carbide, titanium diboride, boron nitride, dysprosium oxide, iron (III) oxide-hydroxide, iron oxide, manganese oxide, titanium dioxide, boron carbide, aluminum nitride, or any combination thereof.

The structural features of the nanostructures can vary depending upon the application. In one aspect, the nanostructure has a diameter from 5 nm to 100 nm, 10 nm to 100 nm, 20 nm to 100 nm, or 30 nm to 100 nm. In another aspect, the nanostructures have a length of 1 to 20 microns, 5 to 20 microns, or 10 to 20 microns. In a further aspect, the nanostructures have a length-to-diameter ratio from 10 to 28,000,000:1.

When the nanostructures are nanotubes, the nanotubes can be either organic nanotubes, inorganic nanotubes, or both. In one aspect, the nanotubes are carbon nanotubes. In certain aspects, the carbon nanotubes can contain amorphous carbon with no clear ordered structure between the atoms as an impurity. Carbon nanotubes

manufactured by SkySpring Nanomaterials, Inc. can be used herein. In one aspect, Single-Walled Carbon Nanotubes (SWNTs) AND Double-Walled Carbon Nanotubes (DWNTs) manufactured by Nanoamor / Nanostructured and Amorphous Materials Inc. can be used herein.

5 In certain aspects, the nanostructures can be functionalized to alter the properties of the reinforced composite. For example, carbon nanotubes can be functionalized with –OH or –COOH groups in order to impart different chemical and mechanical properties to the reinforced composite. Functionalized carbon nanotubes manufactured by SkySpring Nanomaterials, Inc. and Nanoamor / Nanostructured and Amorphous Materials Inc. can
10 be used herein.

 In other aspects, it is desirable to use two or more different types of nanostructures. For example, a carbon nanotube can be used in combination with one or more inorganic nanotubes. In one aspect, the nanostructure includes a mixture of SiO₂ and carbon nanotubes. Not wishing to be bound by theory, the presence of SiO₂ can
15 improve the bonding strength at the interface of the article, which may facilitate the fabrication of the reinforced composites.

 Articles as described herein can include metals or metal sheets. In certain aspects, the article can be selected based on various properties such as, for example, chemical composition, density, tensile strength, stiffness, malleability, electrical conductivity,
20 thermal conductivity, fracture toughness, and coefficient of thermal expansion. In one aspect, each article can independently be a metal sheet. In this aspect, the metal sheet can include, for example, aluminum, iron, nickel, gold, copper, tin, titanium, cobalt, magnesium, platinum, palladium, zirconium, silver, beryllium, an aluminum alloy, an iron based alloy, a nickel based alloy, a copper alloy, a tin alloy, a titanium alloy, a cobalt
25 alloy, a magnesium alloy, platinum alloy, palladium alloy, zirconium alloy, steel, silver alloy, beryllium alloy, brass, a super alloy, or any combination thereof. In one aspect, the first and second articles are, independently, aluminum, iron, silver, beryllium, nickel, copper, tin, titanium, cobalt, magnesium, platinum, palladium, zirconium, an aluminum alloy, an iron based alloy, a nickel based alloy, a copper alloy, a tin alloy, a titanium
30 alloy, a silver alloy, a beryllium alloy, a cobalt alloy, a magnesium alloy, platinum alloy, palladium alloy, zirconium alloy, steel, brass, a super alloy, or any combination thereof.

The first step of the process involves applying the nanostructures to a surface of an article. In one aspect, the nanostructures can be applied to the article by brushing or spraying a dispersion containing the nanostructures onto a surface of the article. The dispersion containing the nanostructures can include a solvent such as, for example, an organic solvent like an alcohol. In certain aspects and after coating the surface of the article with a dispersion containing nanotubes, the article may be dried at room temperature or baked to remove any excess or residual solvent from the coating. If heat is applied, it is low heat and is well below the recrystallization temperature and annealing temperature of the article. Prior to the application of the nanostructures, the surface of the article can be optionally wire brushed, degreased with acetone, or a combination thereof.

The amount of nanostructures applied to the article can vary. In one aspect, nanostructures can be applied to the article such that at least 0.1 g/m^2 to 230 g/m^2 , 0.1 g/m^2 to 200 g/m^2 , 0.1 g/m^2 to 100 g/m^2 , or 0.1 g/m^2 to 60 g/m^2 of nanostructures are on the surface of the article. In one aspect, after being subjected to a final pressure bonding step, the reinforced composite's total weight of nanostructures ranges from 0.01 wt% to 30 wt%, 0.1 wt% to 28 wt%, 0.4 wt % to 26 wt%, 0.75 wt% to 22 wt%, 1 wt% to 20 wt%, 3 wt% to 17.5 wt%, 5 wt% to 15 wt%, 7.5 wt% to 12.5 wt%, or 9 wt% to 11 wt%.

Next, a second article is applied to the coated surface of the first article (*i.e.*, the surface of the first article coated with nanostructures). The first and second articles can be applied to one another by an optional welding step, spot welding step, clamping step, clipping step, physically attaching step, or any combination thereof. In this aspect, the welding step, spot welding step, clamping step, clipping step, physically attaching step, or any combination thereof occurs before the first and second articles are subjected to the pressure bonding step. Depending upon the final application of the reinforced composite, multiple articles can be stacked on one another by using the process described above. Thus, sequential application of the nanostructures on the articles can produce a stacked structure. In one aspect, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, or 40 articles can be stacked on one another with intervening layers of nanostructures followed by pressure bonding to produce a reinforced composite.

After the second article (or multiple articles) has been applied to the first article coated with nanostructures, the layered articles are subjected to pressure bonding. In one aspect, pressure bonding includes roll bonding, forge welding (either hot or cold), ultrasonic welding, diffusion bonding, or a combination thereof. In certain aspects, roll bonding includes feeding the contacted first and second articles into a roll press; and bonding the first metal article to the second metal article by applying pressure to produce the reinforced composite. The amount of pressure and time for pressure bonding the articles may be readily varied and optimized based on the materials being used and the types of reinforced composites being produced. In this aspect, roll bonding may be optimized based on various properties of the articles (e.g. chemical properties, density, tensile strength, malleability, electrical conductivity, and thermal conductivity). For example, the optimal feed rate and the amount of pressure applied (calculated by size or thickness reduction of the article) may be calculated based on these properties. In this aspect, the maximum thickness of the articles used to make the composites described herein are limited only by the separating force capacity of the rolling equipment, the flow strength of the articles used to make the composite, and the rolling speed or feeding rate of the roll bonding machine. A standard equation may be used to estimate maximum thickness, and the lower limit may be determined by the precision of the rolling equipment that controls the separation of the rollers. In one aspect the equation is the following: force, $F = \sigma_y b \sqrt{R \Delta h}$, where σ_y is the yield stress of the metal, b is the sheet width, R is the radius of curvature of the rollers, and Δh is the desired thickness reduction of the sheets.

In one aspect and after producing the initial composite (*i.e.*, stacked articles that have not been subjected to pressure bonding), the composite can be subjected to 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, or more roll bonding steps. The number of roll bonding steps can vary depending upon the number of articles used as well as the nature and amount of nanostructures selected. Not wishing to be bound by theory, the nanostructures (*e.g.*, nanotubes), will align in the

direction of the roller. Thus, it is possible that alternating the direction of rolling in a controlled manner can alter the alignment of the nanostructures, which in turn can alter the properties of the reinforced composite. For example, if the reinforced composite requires good heat dissipation or enhanced electrical conductivity in one direction, the nanostructures can be aligned in a particular direction by rolling in a specified direction.

In other aspects, forge welding (either hot or cold), ultrasonic welding, diffusion bonding, or a combination thereof can be used as the pressure bonding step. Forge welding includes heating the contacted first and second articles and then hammering them together. In this aspect, the two articles are pressure bonded together. Ultrasonic welding involves pressing two components together at high pressure and applying high frequency vibrations that induce relative sliding motion at the interface of the components. The frictional heat and pressure lead to formation of a joint. For example, ultrasonic welding includes applying high-frequency ultrasonic acoustic vibrations to the contacted first and second articles to create a solid state weld. In another aspect, diffusion bonding involves pressing two components at high pressure, and heating them up to just below their melting temperature in a controlled atmosphere. Diffusion of atoms from one component to the other will lead to the formation of a bond.

In certain aspects, pressure bonding aids in refinement of the composite, or more specifically, aids in the refinement of the composite's metal matrix if the composite was produced from a metal based article. In one aspect, this grain refinement can be used to achieve superplastic forming properties in the composites, which may be of great industrial importance. In certain aspects, achieving superplastic forming properties in the composites is of great industrial importance because superplastic deformation will allow near net-shape forging or stamping of components from the material, vastly reducing wasted material and increasing design flexibility.

In this aspect, the nanostructures can be dispersed into the reinforced composite such as, for example, the composite's metal matrix after pressure bonding. For example, a uniform distribution is achieved in the through-thickness direction by increasing the number of rolling steps so that the separation distance between the reinforced layers approaches the length scale of the nanostructures. Good dispersion can be achieved in the planar direction since the rolling cycles will progressively elongate the sheet material

and separate the nanostructures from each other, starting from their rather entangled and agglomerated state before rolling. Good dispersion of nanostructures enables the reinforced composite to have homogenous properties and enhances the mechanical properties of the composite. In another aspect, the pressure bonding step refines the composite's microstructure into a nanocrystalline structure and in certain instances is capable of producing an amorphous structure, which can include a metallic glass structure. A nanocrystalline or an amorphous glass structure provides for increased strength, increased elastic strain values, improved chemical absorption, improved hydrogen absorption, and an improved damping coefficient. In certain aspects within this nanocrystalline or amorphous glass structure, the nanostructures remain substantially unchanged in dimension including diameter and length when compared to the starting material (*i.e.* the initial nanostructures that were applied to the first article). In other aspects, the nanostructures in the final reinforced composite have the same or similar dimensions. For example, when the starting material is carbon nanotubes having a bimodal diameter size distribution, the nanostructures in the final reinforced composite only have nanotubes with diameters greater than 30 nm and greater than 30 walls after four consecutive roll bond operations at 50% reduction. In certain applications, it is desirable that the nanostructures have consistent structures and morphology.

The pressure bonding step does not require the application of heat. Thus, in one aspect, the pressure bonding step is performed at room temperature. However, in certain aspects, heat can be optionally applied to any of the articles including the first and second articles either immediately before or during the pressure bonding step. Heat may allow for optimal pressure bonding conditions and for optimal adherence of the first article to the second article. In this aspect, the heating step includes heating the first and second articles within a temperature range from room temperature up to the recrystallization temperature of any article before or during step (c) for 5 to 30 minutes. For example, the articles can be heated to 20 °C, 25 °C, 30 °C, 35 °C, 40 °C, 45 °C, 50 °C, 55 °C, 60 °C, 65 °C, 70 °C, 75 °C, 80 °C, 85 °C, 90 °C, 95 °C, 100 °C or greater than 100 °C for 5 to 30 minutes either before or during step (c). In one aspect, recrystallization and recovery depend on time, temperature, and material. In certain aspects, heating is required only if

it is necessary to reduce the yield stress of the articles during pressure bonding, or to improve bonding between the articles.

The optional heating step described above is different from annealing the composite. After pressure bonding, the reinforced composite is not annealed. The term “annealed” is defined herein as the temperature that is at least 60% of the melting point of the article used to make the reinforced composite. Annealing temperatures are typically 60% to 95% of the melting temperature of a particular metal. Although annealing can improve ductility and reduce the hardness of a metal, the nanocrystalline structure of the metal matrix cannot be preserved due to coarsening and grain growth of the microstructure. Not wishing to be bound by theory, annealing between and/or after rolling cycles will coarsen the grain structures in the metal matrix. For example, annealing between cycles can cause the hardness of a commercially pure aluminum matrix to be reduced from 69 Vickers to 56 Vickers hardness (*see Examples*).

In certain aspects and after subjecting to pressure bonding, the reinforced composite can once again be optionally coated with additional nanostructures. In this aspect, the reinforced composite can be cut into at least two pieces (*i.e.* a first cut composite and a second cut composite), with a first cut composite again coated with another layer of nanostructures. Then the first cut composite can be stacked onto the second cut composite or vice versa and subjected to a pressure bonding step. Alternatively, the reinforced composite can be optionally coated with nanostructures. Then the reinforced composite, which is either coated with additional nanostructures or not coated with additional nanostructures, is folded onto itself, or otherwise manipulated to produce a multilayered composite. Next, the folded or multilayered composite is subjected to a pressure bonding step. In each aspect, these cut and/or folded reinforced composites can be further subjected to pressure bonding. The process of incorporating the nanostructures and pressure bonding, as described above, may be repeated as many times as needed or desired to obtain an amorphous glass structure or a nanocrystalline structure.

The methods and composites described herein are advantageous because each reinforced composite can be produced efficiently and relatively inexpensively using

conventional equipment with minimal damage to the nanostructures without voids in certain areas of the composite, and without the use of complex processing techniques such as ball milling, sintering, or electrodeposition. In one aspect, the methods described herein can be conducted at room temperature, which will limit the degradation of the nanotubes.

In general, the reinforced composites described herein are resistant to deformation and have high thermal and electrical conductivity. These features make the composites very useful in several different applications. In certain aspects, the compositions described herein can be used for vibrational damping. The reinforced composites described herein exhibit a very high damping (or loss) coefficient or internal friction properties. For example, the internal friction coefficient of a commercially pure aluminum matrix is increased from 0.00279 to 0.0132 when a concentration of 0.4 wt% of carbon nanotubes is added to the alloy in the first step and roll bonding is carried out for 3 rolling cycles without annealing. These characteristics are useful for noise canceling materials and may be used in certain types of instrumentation. In one aspect, the reinforced composites can yield superior acoustic performance in audio speaker applications. The composite sheet material fabricated by the methods described herein can be readily formed into a dome or diaphragm shape. It has been shown that alternating structures of a stiff material sandwiched between lower stiffness material has good vibration damping properties. This concept is used in sound absorbing materials and windows (*see* Hart et al. U.S. Patent 4,599,261; Keller, Glass Processing Days, 18–21 June 2001, session 32, p. 735). The improved damping will reduce the inherent vibration or ‘ringing’ of the speaker, and consequently reduce the distortion to yield higher fidelity. Another key requirement for extending the frequency and bandwidth of a speaker before distortion is high stiffness, which is another feature of the reinforced composites described herein as they have exceptionally high Young’s modulus. The reinforced composites also have increased heat conductivity, which improves the maximum power handling of the speaker before thermal damage occurs at high sound amplitudes.

In other aspects, the reinforced composites can provide a unique combination of improved ballistic and blast resistance for metallic armor plate. The reinforced

composite can be produced in a thick plate itself. In the alternative, a thin layer of the composite can be roll bonded onto other thicker plates of armor to provide further enhancement of performance. It has been shown that layered structures improve the performance of armor since the interfaces between the different materials cause damping of the shockwaves produced during impact, due to elastic wave reflection and deflection (Park et al., International Journal of Solids and Structures 42 (2005) p. 123, Grujicic et al. Applied Surface Science 253 (2006) p. 730). In one aspect, a sheet (approx 1 mm thick) of the roll bonded composite can be applied to thicker aluminum or even steel armor by roll bonding itself in the final rolling cycle at low cost and low weight. Protective cladding layers are commonly roll bonded for dissimilar metals in the pressure vessel industry for corrosion protection. This could offer improved blast and ballistic performance, it should be noted that both of these scenarios (blast, and ballistic) impose different loading conditions and are to improve simultaneously.

In other aspects, the composites described herein can be incorporated into a structural sheet material. Due to the high strength to weight ratio and high stiffness to weight ratio, the composites described herein can be used as structural sheet materials in transportation and construction industries. For example, the automotive industry relies on the use of exterior body panels and interior structural panels stamped from sheet metal. The aerospace industry uses high strength aluminum alloy skin materials. In both cases the materials are on the order of ~1 mm thick. The reinforced composites described herein can be used in these applications since some formability can be retained and large sheets can be readily produced using the methods described herein.

EXAMPLES

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the articles, compositions, and methods described and claimed herein are made and evaluated, and are intended to be purely exemplary and are not intended to limit the scope of what the inventors regard as their invention. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.) but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight and temperature is in °C and is at

ambient temperature. There are numerous variations and combinations of reaction conditions, e.g., component concentrations, desired solvents, solvent mixtures, temperatures, pressures and other reaction ranges and conditions that can be used to optimize the product and yield obtained from the described process. Only reasonable and routine experimentation will be required to optimize such process conditions.

Example 1

A metal matrix composite reinforced with carbon nanotubes was fabricated by the method shown in Figure 1. A uniform coating of carbon nanotubes was applied on the surface of an aluminum metal sheet. The coated sheets were subsequently subjected to repeated roll bonding. After roll bonding, carbon nanotubes were confirmed by transmission electron microscopy (TEM) to have survived multiple roll bonding operations and were embedded in the aluminum matrix as shown in Figure 2.

Preliminary trials involved roll bonding with only 1 layer of carbon nanotubes, and then repeating the rolling cycle 3 additional times. All tests were conducted on a 4" diameter x 6" wide rolling mill with a 50% thickness reduction per pass and constant rolling speed of 21.7 m/min, or 0.362 m/s. The weight percent of carbon nanotubes is 0.0059% using 1 mm thick sheets of aluminum. The maximum carbon nanotube concentration that can be achieved is dependent on the thickness of the metal sheets, and the limiting concentration of carbon nanotubes between the sheets per pass that will facilitate bonding. Using the current technology to disperse the carbon nanotubes in 4 passes (15 layers of carbon nanotubes when carbon nanotubes are added before each rolling pass), a concentration of 0.024 wt% was achieved. Preliminary tests used bundled carbon nanotube material (with lengths of 10 to 20 μm), and there was evidence to suggest that the roll bonding process actually provided some dispersion of the carbon nanotube bundles. A more uniform coating of carbon nanotubes may be achieved with easily dispersible (1 to 2 μm) carbon nanotube material.

In other experiments, the concentration of the carbon nanotubes can be up to 0.4 wt% in a 0.4 mm sheet when the carbon nanotubes are added in only the first pass and stacked and roll bonded for a total of 3 passes.

Chemical analysis by inductively coupled plasma (ICP) spectrometry for an aluminum alloy base material sheet is shown in Table 1. Table 1 shows the chemical

composition in wt% of the aluminum alloy sheets used during roll bonding. The carbon nanotube reinforced layer was examined by transmission electron microscopy (TEM) (Figure 2), and the selected area electron diffraction pattern (Figure 3) shows spot patterns corresponding with the crystalline aluminum and rings corresponding with the carbon nanotube phase. As shown in Figure 3, the separation distances along different crystal directions for the carbon atoms in the nanotubes are 3.50, 2.11, and 1.22 Å respectively. As shown in Figure 4, the analysis of the carbon nanotube diameters in the as-received material revealed a bimodal distribution with two size populations: one averaging 20-25 nm, and one around 40-45 nm. The analysis of the roll bonded carbon nanotube composite shows that the population with larger diameters survived multiple rolling cycles.

Table 1

Manganese	0.03%
Silicon	0.08%
Copper	0.13%
Zinc	<0.01%
Iron	0.51%
Beryllium	<0.1%

Key features of the roll-bonding method for producing carbon nanotube reinforced metal matrix composites, was that the structure of the carbon nanotube material was retained during the rolling process, and that the aluminum matrix was refined to a nanocrystalline structure. Figures 2 and 3 shows the roll bonded composite which was passed through the rolling mill 4 times. Grains of aluminum are shown which are <100 nm in diameter, and a large number of carbon nanotubes observed retained their multi-walled structure (as indicated by the first ring on the diffraction pattern) during the rolling process. Most of the other techniques for producing CNT composites (for example, by powder sintering) do not produce a fine grained matrix, and often require extensive ball milling that damages the nanotube structures.

Example 2

Experimental

The sheet material used during roll bonding was a commercial pure aluminum alloy (AA1100) with a composition of Al-0.51Fe-0.13Cu-0.08Si-0.03Mn. The as-received aluminum consisted of a fully annealed microstructure with an equiaxed average grain size of 52 μm , and was cut into 150 x 25 x 1.4 mm strips. Multiwalled CNTs were ultrasonically agitated in 2-propanol or methanol, and then heated in order to evaporate the alcohol and obtain a highly concentrated suspension of CNTs. After degreasing the aluminum and wire brushing the surfaces, the sheets were coated once with the concentrated CNT suspension and allowed to dry. The sheets were then stacked together making a 2.8 mm thick sandwich that was accumulatively roll-bonded 4 times at room temperature with intermediate degreasing and wire brushing as indicated in Figure 1. The diameter of the rollers was 100 mm, the rolling speed was 75 rpm, and the thickness reduction was 50% during each pass. It should be noted that the aluminum sheets were only coated with CNT material once in order to determine the influence of mechanical loading on nanotubes all exposed to the same number of rolling cycles.

TEM was used to study the microstructure of the metal matrix composite. The TEM samples were prepared from 3 mm disks which were punched out from the plan view of the sheet and mechanically thinned. These were then electropolished using a solution of 25 vol.% of HNO_3 and 75 vol.% of methanol at a temperature of -35°C and voltage of 12 V, and examined using a JEOL 2010 microscope operating at 200 kV. Samples which were observed along the transverse plane of the sheet were sectioned using electrical discharge machining before electropolishing.

Results and Discussion

Aluminum Matrix and CNT microstructures

Figure 5 shows the morphology of the as-received CNTs which ranged in diameter from 10 to 70 nm, and a nominal axial length of 10 to 20 μm . Due to their length and morphology, the as-received CNT material was highly entangled.

The microstructure of the CNTs and matrix grains in the composite material following 4 rolling passes are shown in Figure 6 and 7. The repeated rolling cycles produced an ultra fine grained matrix consisting of high-angle boundaries with grain sizes ranging from 100 to 500 nm in the rolling direction. However in the normal direction (ND) of the sheet, the grains with thicknesses of <100 nm could readily be observed, see Figure 7b. The grains were not completely equiaxed and exhibited some elongation in the rolling direction.

The selected area diffraction pattern in Figure 6 indicates the aluminum matrix comprised mostly high angle grain boundaries. The subgrain structure remains after 2 cycles, but the dislocation density increases. Following 3 roll-bonding cycles the dislocation density is dramatically reduced and grains show broad contours within them that suggest high internal stress. At this stage subgrains are still dominant; however some of their boundaries are well-developed and have large misorientations. An ultra fine grained structure with primarily high angle grain boundaries becomes dominant after 4 cycles of roll-bonding. This ultra fine grained microstructure is indicated by the dense and nearly continuous distribution of spots in the diffraction patterns, which is consistent with the selected diffraction pattern shown in Figure 6a. The combination of accumulative roll-bonding differs from previous studies of roll-bonding alloy sheets with CNT powders, since the final structure was not repeatedly rolled a minimum of 4 passes each at 50% reduction, otherwise the final matrix structure will consist primarily of subgrains.

Due to non-uniform strain distributions which may occur during rolling, the distribution of high angle grain boundaries and grain thickness may vary depending on the thickness location. Typically, larger shear strains are produced in the near surface region, and this effect is particularly enhanced when no lubrication is used during rolling. As a result, the grain size is typically finer near the surface due to a higher amount of shear strain, resulting in a larger amount of accumulated dislocations and grain subdivision. Strain gradient and strain path during deformation appear to play a role in the formation of geometrically necessary dislocations and ultra fine grain sizes.

In the case of ARB, the shear strain localized at the surface of any individual pass is distributed during subsequent stacking or folding operations, hence the distribution of deformation eventually becomes uniform with increasing the number of cycles. However the grain size is also influenced by recrystallization and growth resulting due to an
5 adiabatic temperature rise during rolling. Consequently, although ARB is useful in achieving a more uniform structure through the thickness of the sheet, there may ultimately be a limiting grain size for a given material regardless of how many passes are imposed.

The three rings observed in diffraction pattern in Figure 6a are corresponding with
10 the multiwalled CNTs. The average measured d-spacing values for the three diffraction rings observed were 3.50, 2.11, and 1.22 Å, which are within 1% of the spacing values observed for the (002), (004), and (110) Miller indices of the hexagonal unit cell for CNTs. The first and most intense ring corresponds well with the reflections observed for the graphene spacing found in multiwalled CNTs, confirming that these are present in the
15 composite. EDX analysis was conducted on Figure 6b revealed strong Al and C peaks for the composite material.

Hardness increase in the reinforced layers

The samples were cross-sectioned in the transverse direction and the Vickers microhardness was determined at the reinforced interfaces containing the carbon
20 nanotube material in a composite containing 0.2wt% carbon nanotubes. At least 4 measurements were taken with a 10 g load, and a 15 second dwell time. For comparison, the average hardness of the interfacial layers were also measured when 20 nm diameter silicon oxide nanoparticles were used as the reinforcing material with the same concentration. The average hardness observed for the carbon nanotube reinforced layers
25 was 62.7 ± 3.9 HV, while the silicon oxide reinforced layers and aluminum matrix were 58.8 ± 3.8 HV and 56.1 ± 2.8 HV respectively.

Internal friction measurement of the roll bonded composite sheets

The samples were tested as per ASTM E1876 in order to determine the internal friction coefficient and vibration damping capacity of the roll bonded materials. Composite
30 sheets ranging in thickness from 0.35 to 0.5 mm were produced, and compared to

commercially pure aluminum of similar thickness. The commercially pure aluminum has an internal friction coefficient of 0.00279, while a roll bonded sample which was produced with a concentration of 0.4wt% carbon nanotubes added in the initial rolling cycles and roll bonded for a total of 3 rolling cycles without intermediate annealing had
5 internal friction coefficient of 0.0132. This 4.7 times increase in vibration damping capacity results from the combination of a refined matrix microstructure and the presence of several reinforcing layers of carbon nanotubes.

CNT orientation and adhesion at the interface

The properties of CNTs are dependant on their orientation, and so this was
10 investigated by mechanically delaminating the sheets following roll-bonding, and observing the CNTs dispersed between the sheets. This was done by mechanically delaminating and peeling apart the sheets following the roll-bonding operation and examining the surface using SEM, as shown in Figure 8. Although the CNTs were more dispersed than in the as-received material, some entangled bundles of CNTs could also be
15 observed (*see* Figure 8a). The surface revealed a non-uniform distribution of CNTs which were mostly aligned flat to the surface of the sheet (*see* Figure 8b). There was also evidence of aluminum fracture surfaces created by the delamination, since metallic bonding between the aluminum sheets is promoted during roll-bonding.

Since the delamination process may disrupt the CNTs from their original
20 orientation, a cross-section was also heavily etched with HF to expose the CNTs. The sheet interfaces are revealed due to preferential etching, allowing removal of the aluminum material from the sheet interfaces and avoiding mechanical disruption their arrangement. Figure 9a shows the CNTs at the interface, with the majority of CNTs axially aligned in the RD or TD directions. Some of the CNTs were observed to emerge
25 from the aluminum matrix, indicating that there was intimate contact promoted between the CNTs and the aluminum (*see* Figure 9b). This suggests that adhesion has been promoted between with the surrounding matrix.

Rupture of CNTs during rolling

By optimizing the distribution of CNTs and uniformity of the matrix
30 microstructures demands repetitive rolling of the sheets. A highly uniform distribution of

nanotubes in the through-thickness direction provided that CNTs are only introduced once before the initial rolling cycle, and several cycles are applied. For example, since the number of reinforced layers increases exponentially during repeated processing, the number of CNT reinforced layers is equal to (2^{n-1}) , where n is the number of roll bonding cycles. Hence the resistance of the CNTs to rupture is key to achieving a uniform distribution of reinforcement in the final composite.

Alternatively, another key feature of the ARB fabrication process is that it may permit the concentration of CNTs to be increased by repeatedly producing an additional reinforced layer between the stacked sheets prior to each rolling cycle. A prerequisite for the fabrication process is for the majority of nanotubes to remain intact during repeated rolling in order to achieve a satisfactory yield in the final bulk composite. To assess the integrity of the CNTs during rolling, the diameters were measured for 110 nanotubes in the as-received material, as well as for 117 nanotubes subjected to 4 rolling cycles.

The as-received CNTs clearly exhibit a bimodal size distribution in terms of their diameters (Figure 4). This may occur depending on the synthesis route taken to fabricate the multiwalled CNTs. Following 4 roll-bonding cycles, the CNTs with diameters approximately >30 nm appear to have been retained in the composite. Multiwalled CNTs with larger diameters may sustain larger strains when subjected to radial compression. In addition, the larger CNTs in the base material also tended to have a higher apparent wall thickness (see Figure 10a), which indicates these consisted of a greater number of walls. It has been shown using continuum mechanics that the critical buckling stress during radial loading of a multiwalled CNT will increase with the number of walls since the pressure is more evenly distributed over a greater number of walls. As shown in Figure 9, one can assume that the primary loading condition during rolling is compressive loading along the radial direction of the CNTs. Consequently, it is not surprising that the population of CNTs which survived most readily are those which have greater wall numbers, corresponding with those that also had outer diameters >30 nm (Figure 10b).

However, one other property of multiwalled CNTs is that the radial buckling stress of the CNTs should increase as the inner diameter decreases. In contrast the CNTs which had a smaller inner radius did not survive the loading cycles during rolling in the

present work. It is possible that this may be accounted for by the biaxial loading conditions imposed during rolling. Due to the mismatch in the yield strength and stiffness of carbon nanotubes versus aluminum, CNTs are exposed to high axial tensile stresses during the rolling process. The axial tensile stress which contributes to buckling is lower in CNTs with a larger diameter since these have a higher number of walls and there is a greater effective cross-sectional area. Under the same loading conditions during rolling, there will be more pressure on CNTs having smaller diameter. The buckling process is a precursor to rupture of the CNTs since the formation of kinks and defects occurs during buckling, ultimately leading to failure. Hence the CNTs which have prematurely buckled are not likely to survive the rolling process.

Evidence of ruptured CNTs could be found using by TEM and EDX analysis. The chemical composition was measured at the 3 points showing in Fig. 9 and the results are given in Table 2. A progressively decreasing fraction of carbon could be detected at points further from the end of the broken CNT. This indicates the presence of carbon in locations of the aluminum matrix devoid of CNTs. In previous studies it has been shown that the results of these ruptures would be formation of highly defected carbon structures such as graphite layers (DS Tang, LC Chen, LJ Wang, et al. (2000) J Mater Res 15:560), these may dissociate into the aluminum matrix and form a solid solution with carbon contents similar to that observed in point C in Figure 11. It is suggested that this carbon was contributed primarily by the CNTs with diameters <30 nm that ruptured during rolling.

Table 2: EDX quantification in at% measured at points A, B and C of Figure 9.

Point	Al	C	Si	Fe	Cu	Ca
A	68.0	30.82	0	0.4	0.77	
B	76.71	18.05	0	0.06	0.79	4.41
C	94.4	2.21	0.02	0.59	0.87	1.92

Conclusion

In conclusion, it has been shown that a modification of the accumulative roll-bonding may be used to disperse CNTs into an aluminum alloy. The process was effective in producing a composite microstructure with multiwalled CNTs embedded in

an ultra fine grained aluminum matrix. The CNTs with diameters >30 nm and more than 30 walls readily endured 4 consecutive roll-bonding operations, and their multiwalled structure was preserved in the final composite.

5 It is to be understood that the above-described compositions and modes of application are only illustrative of preferred embodiments of the present invention. Numerous modifications and alternative arrangements may be devised by those skilled in the art without departing from the spirit and scope of the present invention and the appended claims are intended to cover such modifications and arrangements. Thus, while the present invention has been described above with particularity and detail in connection
10 with what is presently deemed to be the most practical and preferred embodiments of the invention, it will be apparent to those of ordinary skill in the art that numerous modifications, including, but not limited to, variations in size, materials, shape, form, function and manner of operation, assembly and use may be made without departing from the principles and concepts set forth herein

What is claimed:

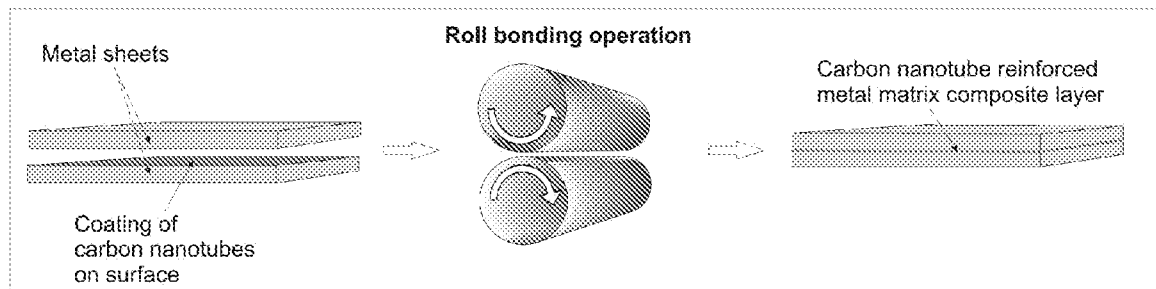
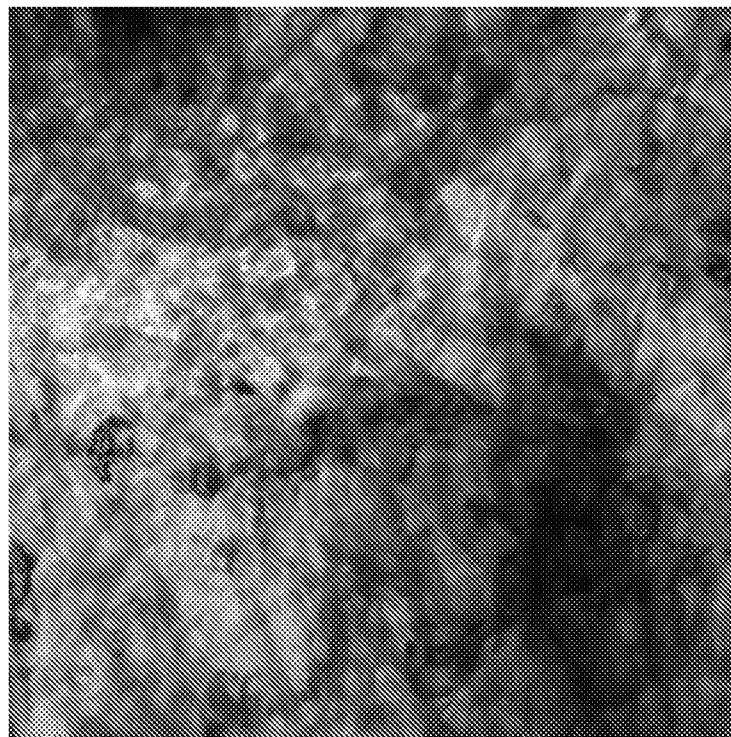
1. A reinforced composite produced by the process comprising:
 - (a) applying nanostructures to a surface of a first article;
 - (b) applying a second article to the surface of the first article comprising the nanostructures; and
 - (c) pressure bonding the first article and second article to produce the reinforced composite,wherein the reinforced composite is not subsequently annealed after step (c).
2. The composite of claim 1, wherein during step (c) the reinforced composite is not heated during pressure bonding.
3. The composite of claim 1, wherein the first and second articles comprise a metal sheet.
4. The composite of claim 1, wherein the first and second articles independently comprise aluminum, iron, nickel, gold, copper, tin, titanium, cobalt, magnesium, platinum, palladium, zirconium, silver, beryllium, an aluminum alloy, an iron based alloy, a nickel based alloy, a copper alloy, a tin alloy, a titanium alloy, cobalt alloy, magnesium alloy, platinum alloy, palladium alloy, zirconium alloy, steel, brass, a silver alloy, a beryllium alloy, a super alloy, or any combination thereof.
5. The composite of claim 1, wherein the first and second articles are, independently, aluminum or an aluminum alloy.
6. The composite of claim 1, wherein step (a) comprises:
 - (i) brushing or spraying a dispersion containing the nanostructures onto the surface of the article; and
 - (ii) drying or baking the coated article produced after step (a).
7. The composite of claim 1, wherein the nanostructure comprises nanotubes, nanowires, nanorods, or any combination thereof.

8. The composite of claim 1, wherein the nanostructure comprises an organic nanotube, an inorganic nanotube, or a combination thereof.
9. The composite of claim 1, wherein the nanostructure comprises an inorganic nanotube, and the inorganic nanotube comprises boron, molybdenum, tungsten, silicon, titanium, copper, bismuth, tungsten carbide, aluminum oxide, titanium dioxide, molybdenum disulphide, silicon carbide, titanium diboride, boron nitride, dysprosium oxide, iron (III) oxide-hydroxide, iron oxide, manganese oxide, titanium dioxide, or any combination thereof.
10. The composite of claim 1, wherein the nanostructure comprises a carbon nanotube or a nanotube containing carbon.
11. The composite of claim 8, wherein the nanotubes have a diameter from 5 nm to 100 nm.
12. The composite of claim 8, wherein the nanotubes have a diameter from 30 nm to 100 nm.
13. The composite of claim 8, wherein the nanotubes have a length from 1 to 20 microns.
14. The composite of claim 8, wherein the nanotubes have a length-to-diameter ratio from 10 to 28,000,000:1.
15. The composite of claim 8, wherein the amount of nanotubes applied to the first article in step (a) is sufficient to produce at least 0.1 g/m^2 to 230 g/m^2 of nanotubes on the surface.
16. The composite of claim 8, wherein after step (c) the nanotubes comprise from 0.01 wt% to 30 wt% of the reinforced composite.
17. The composite of claim 1, wherein the nanostructure comprises a carbon nanotube or a nanotube containing carbon having a diameter from 5 to 100 nm, a length from 1 to 20 microns, and a length-to-diameter ratio from 10 to 28,000,000:1.
18. The composite of claim 1, further comprising prior to step (c) a contacting step, wherein the contacting step comprises welding, spot welding, clamping, clipping,

physically attaching, or any combination thereof the first article to the second article.

19. The composite of claim 1, wherein the pressure bonding step comprises roll bonding, forge welding, ultrasonic welding, diffusion bonding, or any combination thereof.
20. The composite in any preceding claim wherein the pressure bonding step comprises roll bonding at room temperature.
21. The composite of claim 1 further comprising
 - (d) optionally coating at least one surface of the composite produced in step (c) with additional nanostructures;
 - (e) cutting the composite produced in either steps (c) or (d) to produce at least a first cut composite and a second cut composite;
 - (f) stacking the first cut composite onto the second cut composite produced in step (e); and
 - (g) pressure bonding the stacked cut composites.
22. The composite of claim 1 further comprising
 - (d) cutting the composite produced in step (c) to produce at least a first cut composite and a second cut composite;
 - (e) optionally coating at least one surface of the first cut composite or second cut composite produced in step (d) with additional nanostructures;
 - (f) stacking the first cut composite onto the second cut composite produced in either step (d) or (e); and
 - (g) pressure bonding the stacked cut composites.
23. The composite of claims 21 or 22 further comprising repeating steps (d)-(g).
24. The composite of claim 1 further comprising
 - (d) optionally coating at least one surface of the composite produced in step (c) with additional nanostructures;

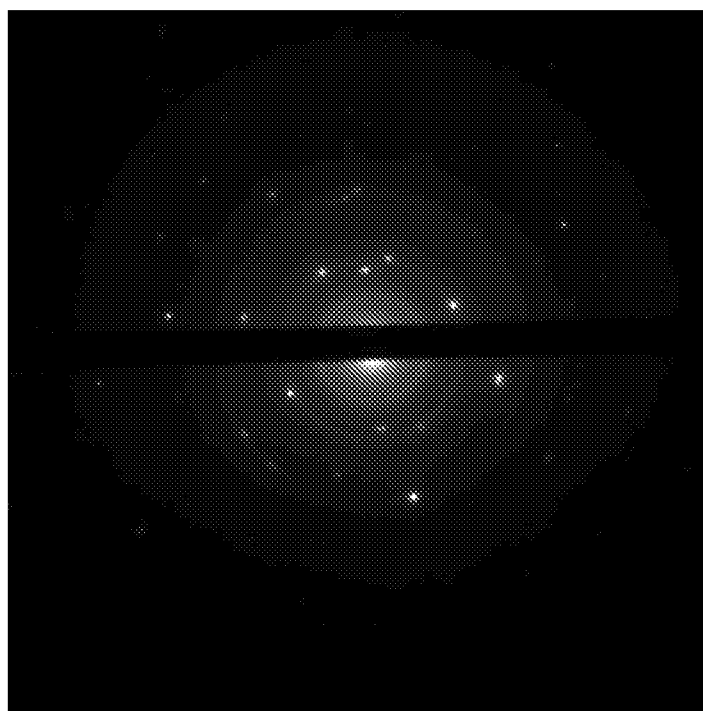
- (e) folding the composite produced in either step (c) or (d) onto itself; and
 - (f) pressure bonding the composite produced in step (e).
25. The composite of claim 1 further comprising
- (d) folding the composite produced in step (c) onto itself;
 - (e) optionally coating at least one surface of the composite produced in step (d) with additional nanostructures; and
 - (f) pressure bonding the composite produced in either step (d) or (e).
26. The composite in claims 24 or 25, further comprising repeating steps (d)-(f).
27. The composite in claims 21-26 wherein the amount of nanostructures present in the composite after the pressure bonding step comprises from 0.01 wt% to 30 wt% of the reinforced composite.
28. The composite of claim 1, wherein at least three or more articles are pressure bonded to produce a reinforced composite.
29. The composite of claim 1, wherein at least four or more articles are pressure bonded to produce a reinforced composite.
30. A method for making a reinforced composite comprising:
- (a) applying nanostructures to a surface of a first article;
 - (b) applying a second article to the surface of the first article comprising the nanostructures; and
 - (c) pressure bonding the first article and second article to produce the reinforced composite,
- wherein the reinforced composite is not subsequently annealed after step (c).
31. The use of the composites in any preceding claim in an audio speaker.
32. The use of the composites in any preceding claim for vibrational damping.
33. The use of the composites in any preceding claim in an armor plate.
34. The use of the composites in any preceding claim in a structural sheet material.

**FIG. 1**

Gerlich.230.tif
4 passes
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500 nm
HV=200kV
Direct Mag: 50000x
X: Y: T:
U of A Physics

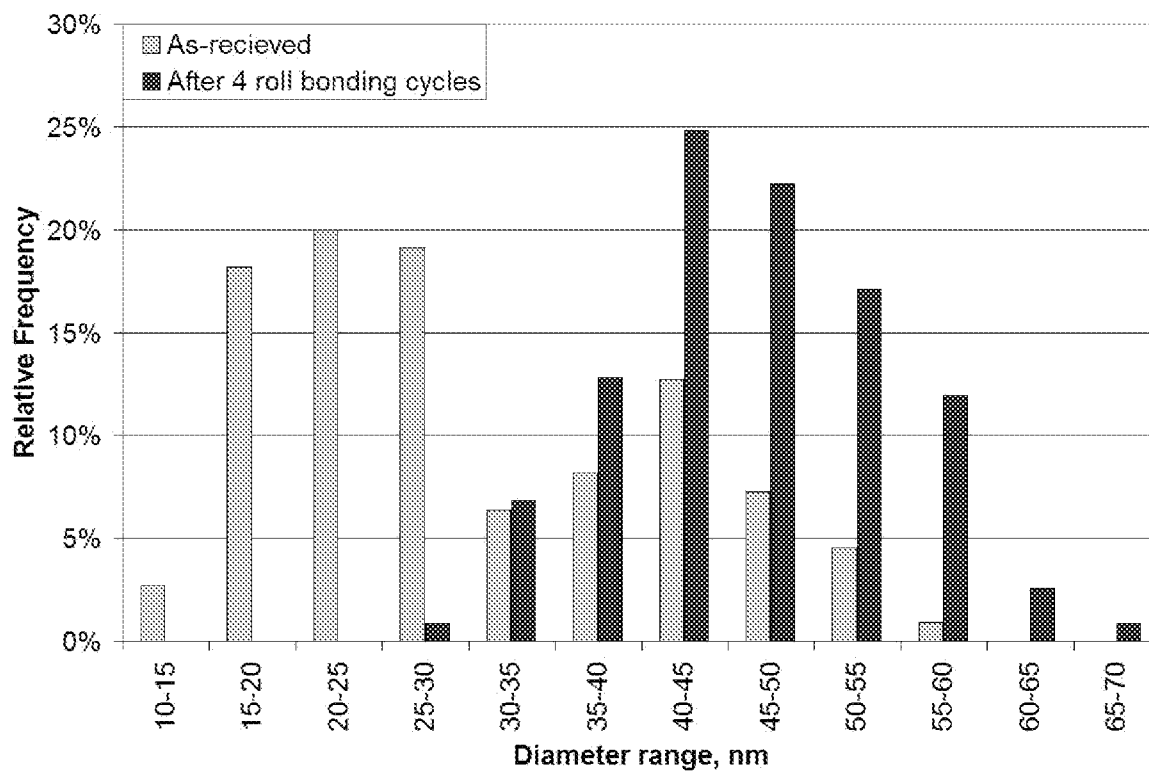
FIG. 2



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.1R
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HV=200kV
Cam Len: 1.0 m
X: Y: T:
U of A Physics

FIG. 3

**FIG. 4**

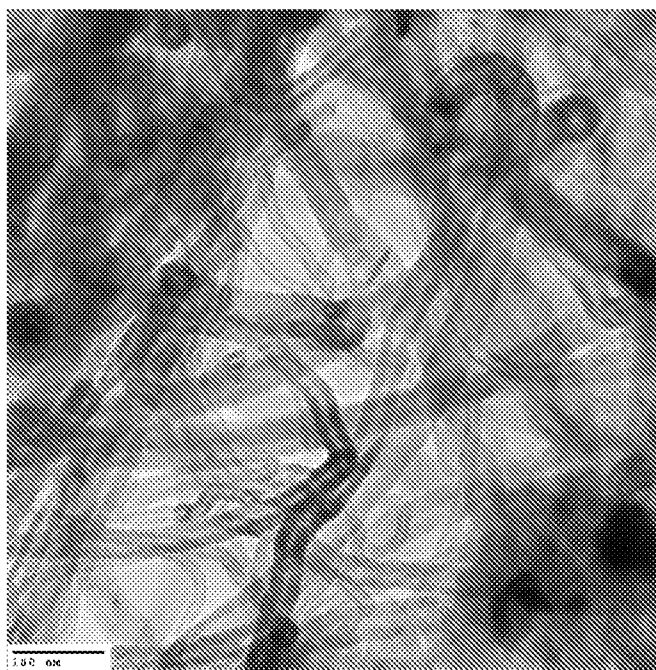


FIG. 5

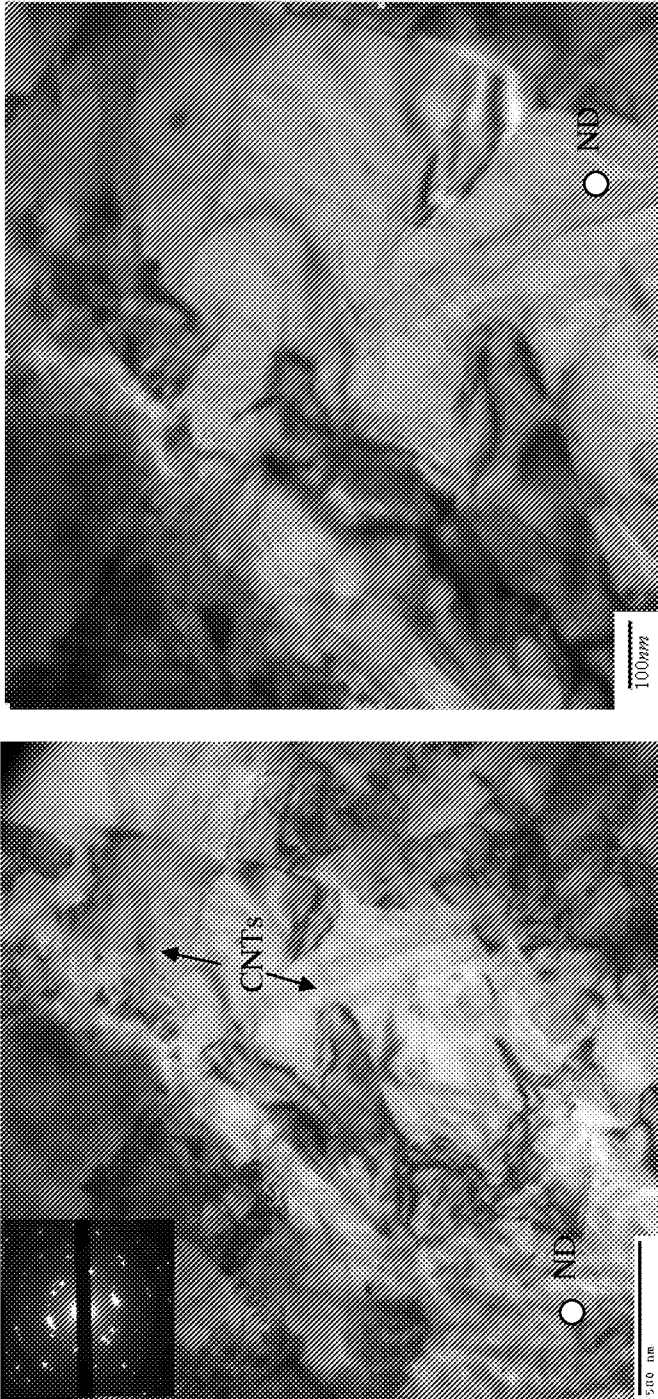


FIG. 6

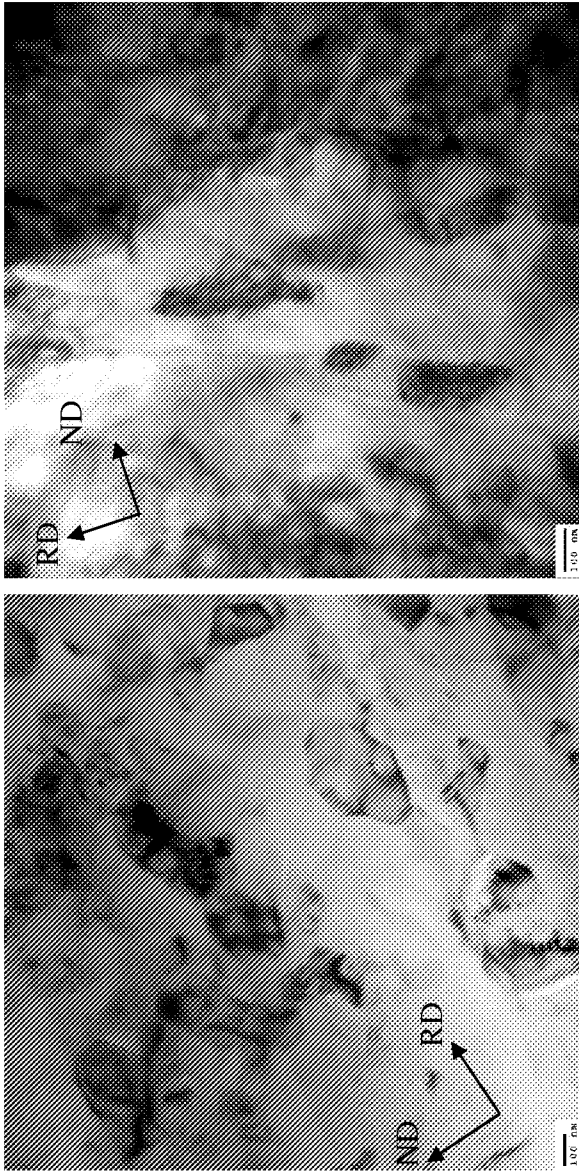


FIG. 7

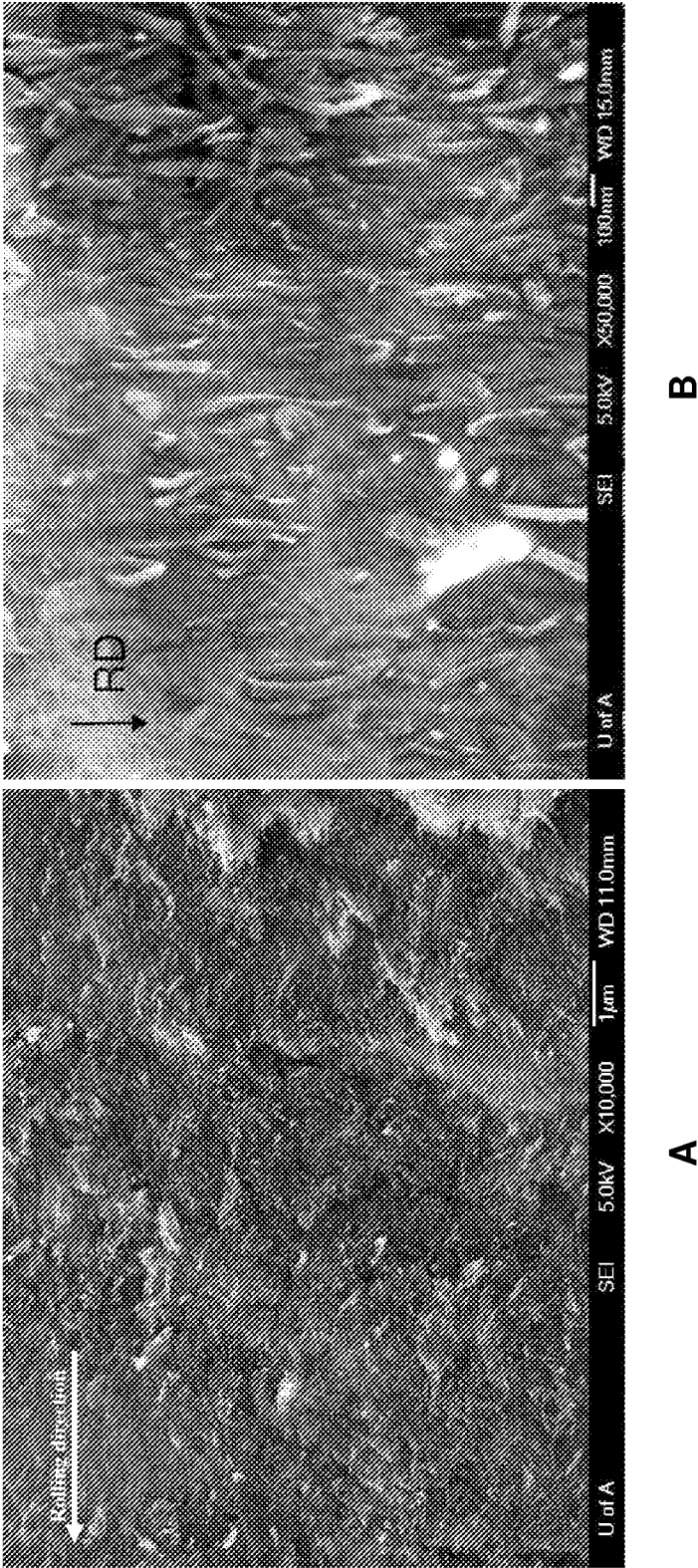
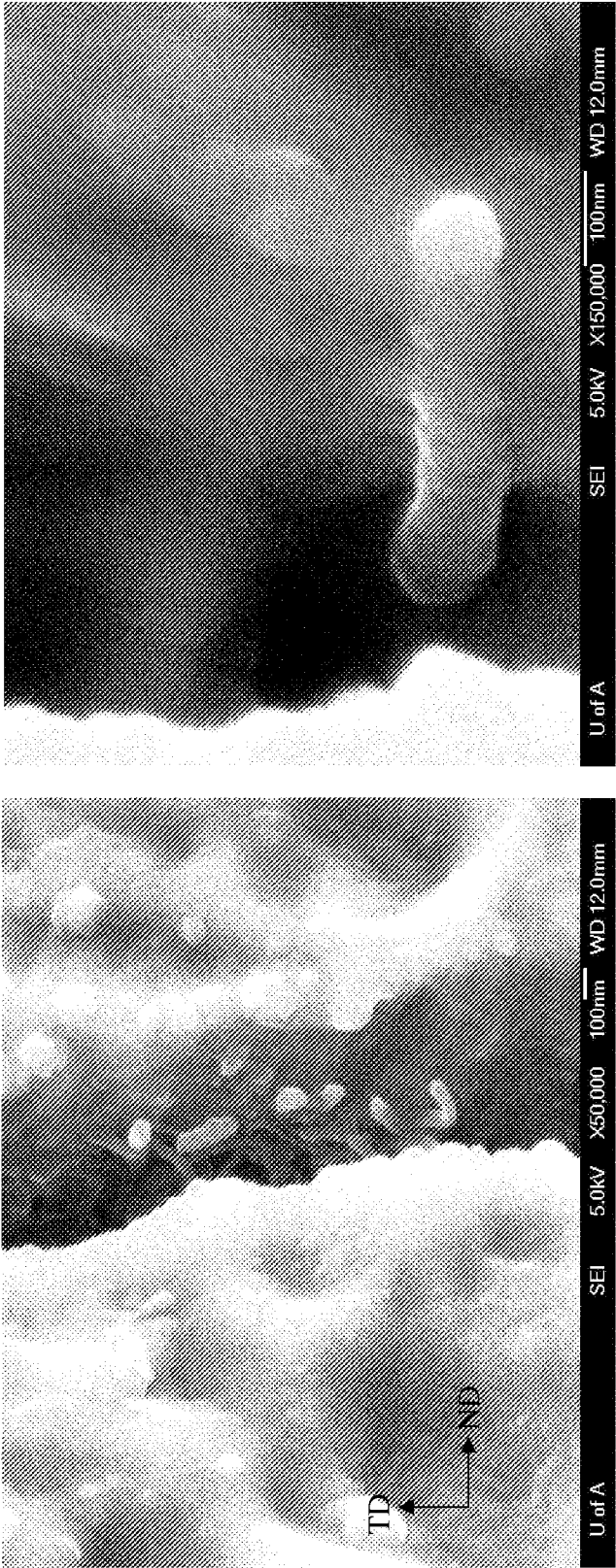


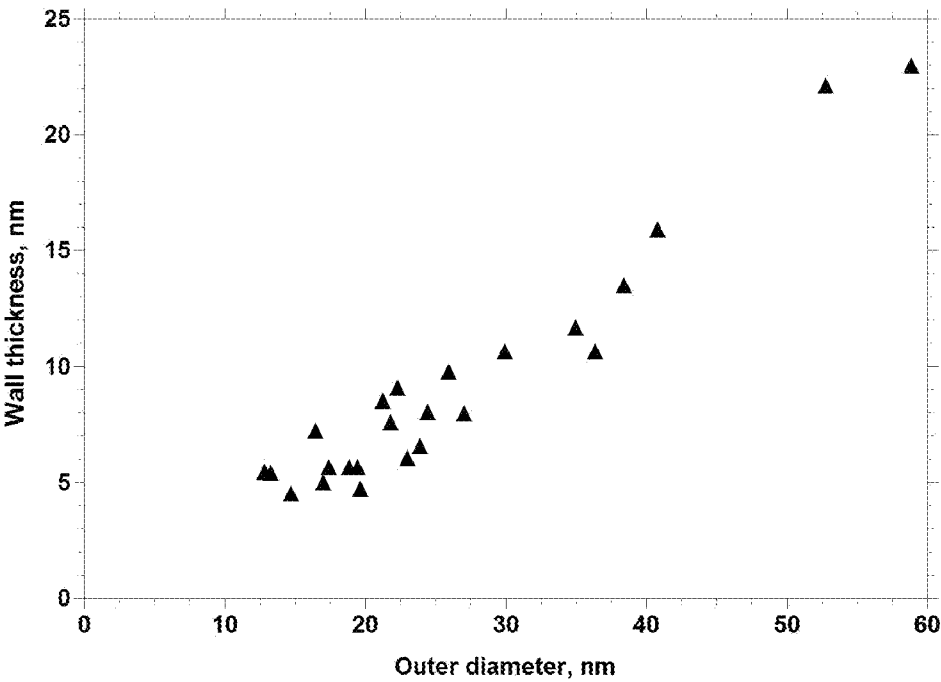
FIG. 8



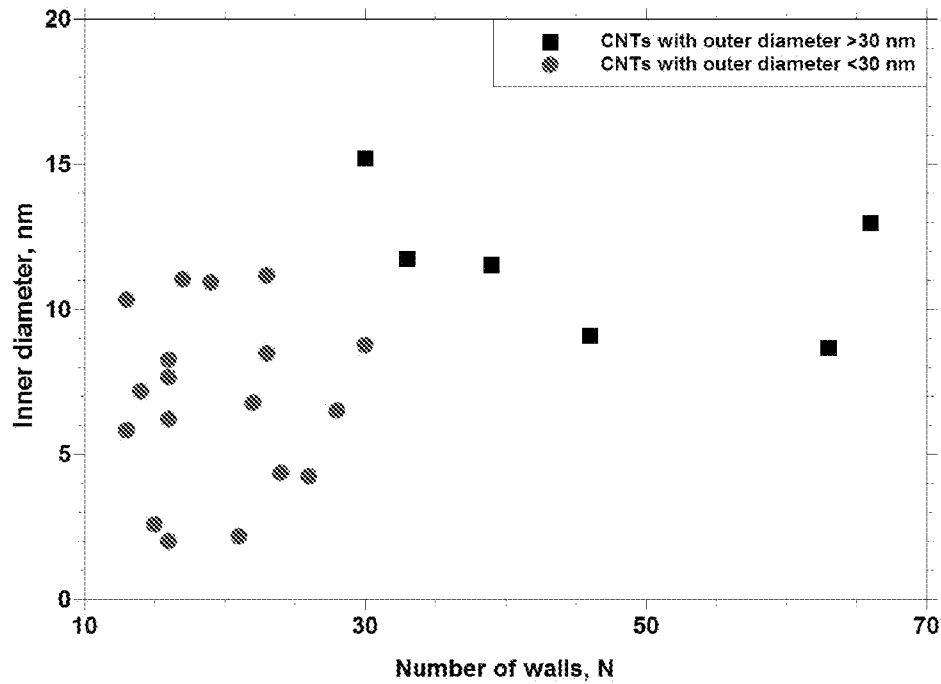
B

A

FIG. 9

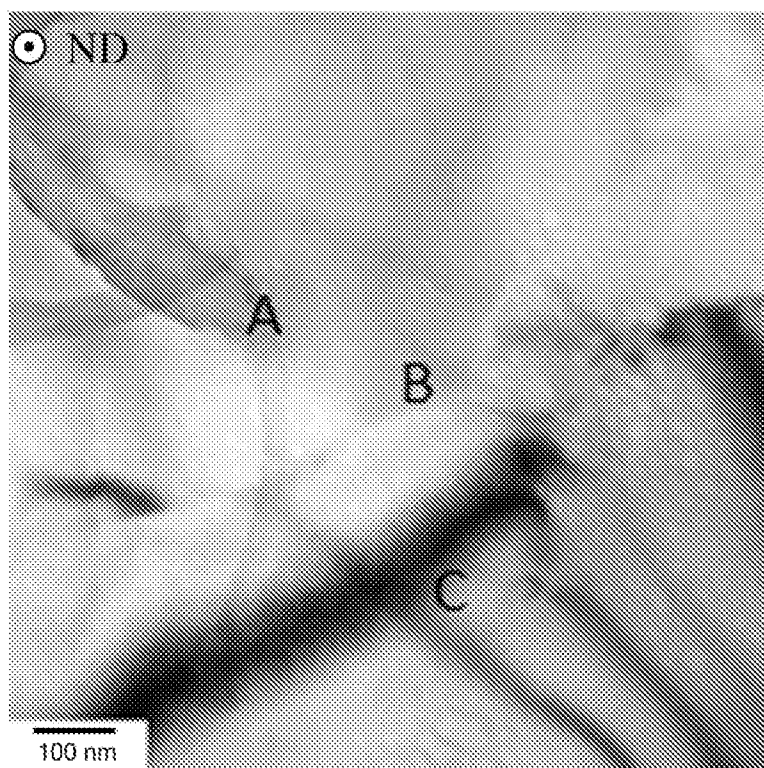
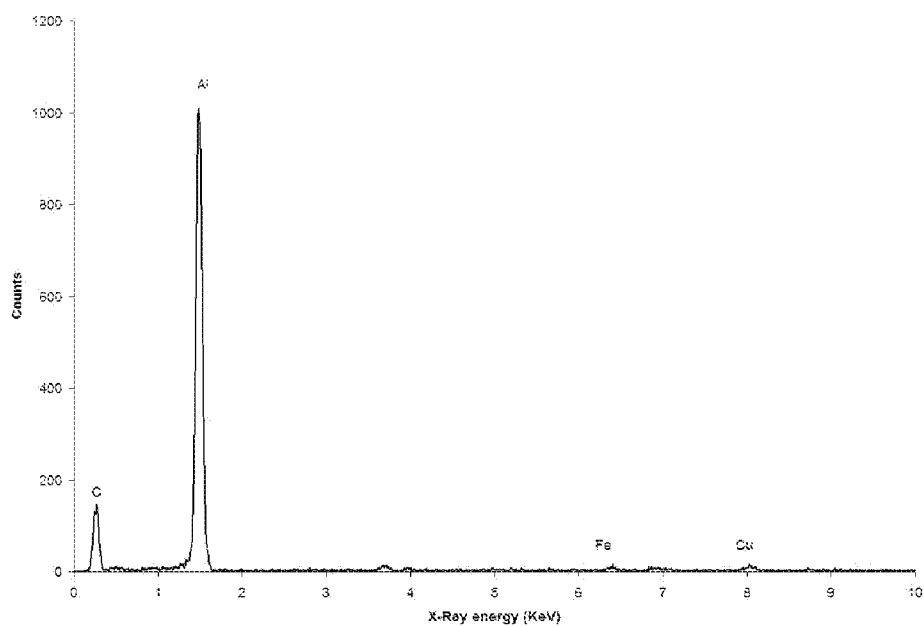


A



B

FIG. 10

**A****B****FIG. 11**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2010/001461

A. CLASSIFICATION OF SUBJECT MATTER IPC: C04B 35/76 (2006.01) , B23K 20/04 (2006.01) , B23K 20/10 (2006.01) , B23K 20/16 (2006.01) , B32B 15/00 (2006.01) , B32B 18/00 (2006.01) (more IPCs on the last page) According to International Patent Classification (IPC) or to both national classification and IPC																				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C04B, B23K, B32B, C22F Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched google scholar Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) SCOPUS, Epoque, Canadian Patent Database reinforced composite, metal matrix composite, nanocomposite, metal sheet, aluminum sheet, nanostructure, nanotube, nanorod, nanowire, carbon nanotube (CNT), roll bond, roll bonding, accumulated roll bonding (ARB), repeated roll bonding (RRB), pressure bonding, forge welding, ultrasound welding, diffusion bonding.																				
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X Y</td> <td>"Cu/Single-walled carbon nanotube laminate composites fabricated by cold rolling and annealing", Nanotechnology, vol.18, pages 1-6, (Yan-Hui Li et al.), April 2007</td> <td>1-8, and 10-29 9, and 30-34</td> </tr> <tr> <td>P, X P, Y</td> <td>"Dual strengthening mechanisms induced by carbon nanotubes in roll bonded aluminum composites", Materials Science and Engineering A, vol. 523, pages 263-270, (S. R. Bakshi et al.) October 2009</td> <td>1-8, and 10-29 9, and 30-34</td> </tr> <tr> <td>A</td> <td>"Carbon nanotube reinforced metal matrix composites-a review", International Materials Reviews, vol. 55, no. 1, pages 41-64, (S. R. Bakshi et al.) January 2010</td> <td>1-34</td> </tr> <tr> <td>A</td> <td>"Synthesis of multi-walled CNT reinforced aluminum alloy composite via friction stir processing", Materials Science and Engineering A, vol. 507, pages 194-199, (D. K. Lim et al.) May 15, 2009</td> <td>1-34</td> </tr> <tr> <td>A</td> <td>"Production of aluminum-matrix carbon nanotube composite using high pressure torsion", Materials Science and Engineering A, vol. 490, pages 300-304, (T. Tokunaga et al.) 2008</td> <td>1-34</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X Y	"Cu/Single-walled carbon nanotube laminate composites fabricated by cold rolling and annealing", Nanotechnology, vol.18, pages 1-6, (Yan-Hui Li et al.), April 2007	1-8, and 10-29 9, and 30-34	P, X P, Y	"Dual strengthening mechanisms induced by carbon nanotubes in roll bonded aluminum composites", Materials Science and Engineering A, vol. 523, pages 263-270, (S. R. Bakshi et al.) October 2009	1-8, and 10-29 9, and 30-34	A	"Carbon nanotube reinforced metal matrix composites-a review", International Materials Reviews, vol. 55, no. 1, pages 41-64, (S. R. Bakshi et al.) January 2010	1-34	A	"Synthesis of multi-walled CNT reinforced aluminum alloy composite via friction stir processing", Materials Science and Engineering A, vol. 507, pages 194-199, (D. K. Lim et al.) May 15, 2009	1-34	A	"Production of aluminum-matrix carbon nanotube composite using high pressure torsion", Materials Science and Engineering A, vol. 490, pages 300-304, (T. Tokunaga et al.) 2008	1-34
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☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex. <table border="1"> <tbody> <tr> <td>* Special categories of cited documents :</td> <td>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"E" earlier application or patent but published on or after the international filing date</td> <td>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"&" document member of the same patent family</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td></td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </tbody> </table>			* Special categories of cited documents :	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family	"O" document referring to an oral disclosure, use, exhibition or other means		"P" document published prior to the international filing date but later than the priority date claimed							
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"O" document referring to an oral disclosure, use, exhibition or other means																				
"P" document published prior to the international filing date but later than the priority date claimed																				
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Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476		Authorized officer Brenda Zhang (819) 934-1348																		

INTERNATIONAL SEARCH REPORT

International application No.
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