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(54) **Title**: CARBON NANOTUBE ENHANCED ELECTRICAL CABLE

(57) **Abstract**: The present invention discloses methods for making CNT-enhanced electrical power cables with improved electrical conductivity, high current density capacity and low specific weight. The cables are made from rolled or folded sheet metal with directly grown-on carbon nanotubes.

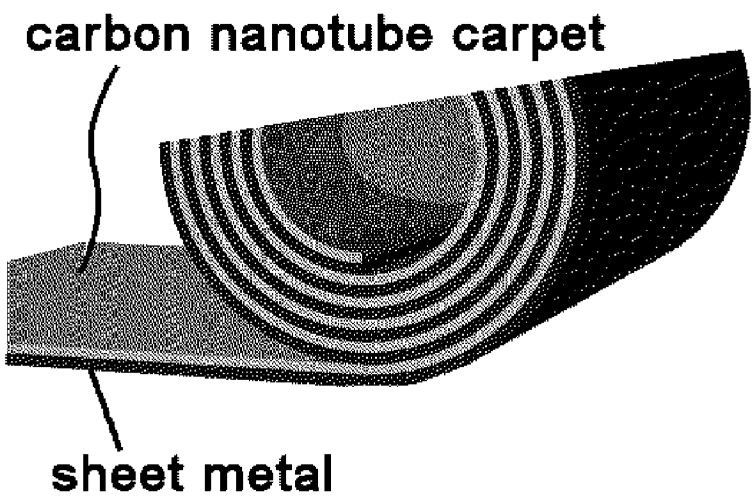

Fig. 1

WO 2013/127444 A1

Description

CARBON NANOTUBE ENHANCED ELECTRICAL CABLE

Technical Field

Technical Field

[0001] Much research has been undertaken in utilizing carbon nanotubes (CNTs) as reinforcement for composite materials. CNT-reinforced metal matrix compounds (MMCs) have received strong attention. These composites are being used in structural applications because of their high specific strength as well as functional materials because of their thermal and electrical characteristics. The present invention discloses methods for making CNT-enhanced electrical power cables with improved electrical conductivity, high current density capacity and low specific weight.

Background Art

Background Art and Technical Problem

[0002] Carbon nanotube reinforced metal matrix (MM-CNT) composites are prepared through a variety of processing techniques. Powder metallurgy is the most popular and widely applied technique for preparing MM-CNT composites. Electrodeposition is the second most important technique for deposition of thin coatings of MM-CNT composites as well as for deposition of metals on to CNTs. For low-melting-point metals such as Mg and bulk metallic glasses, melting and solidification is a viable route.

[0003] Most of the studies on Al-CNT and approximately half of the research work on Cu-CNT composites have been carried out using the powder metallurgy method. A few researchers have also prepared CNT composites based on Mg, Ni, Ti, Ag, Sn, and intermetallics through this route. The basic process steps consist of mixing CNTs with metal powder by grinding or mechanical alloying, followed by consolidation by compaction and sintering, cold isostatic pressing, hot isostatic pressing, or spark plasma sintering. In most of these works, the composite compacts were subjected to post-sintering deformation processes such as rolling, equi-channel angular processing, extrusion, etc. Irrespective of the process steps, the main focus was on obtaining good mechanical reinforcement, by achieving homogeneous dispersion of CNT in the metal matrix and good bonding at the metal/CNT interface.

[0004] Interfacial phenomena and chemical stability of the CNTs in the metal matrix are critical for several reasons. The fiber-matrix stress transfer and the interfacial strength play an important role in strengthening. The applied stress is transferred to the high strength fiber through the interfacial layer, so that a strong interface would make the composite very strong but at the expense of ductility of the composite. A weak interface would lead to lower strength and inefficient utilization of fiber properties by facilitating pullout phenomena at low loads due to interface failure. Wetting of the fiber by the liquid metal is essential. Non-wetting will lead to poor interfacial bonding. Interfacial reactions leading to formation of an interfacial phase can improve wetting if the liquid has a lower contact angle with the phase forming due to the reaction. A lot of work has been carried in reinforcing aluminium matrix with carbon fibers. Interfacial reactions and degree of wetting of the fibers have been shown to affect the properties of the composite. Formation of aluminium carbide (Al_4C_3) has been observed at the interface in liquid metal infiltrated aluminium silicon alloy composites reinforced with carbon fibers. In the case of CNT-reinforced aluminium composites, Al_4C_3 helps in load transfer by pinning the CNTs to the matrix.

[0005] Uniform dispersion of CNTs has been the main challenge in CNT-reinforced composites be they polymer, ceramic or metal matrix. This is due to the fact that CNTs have tremendous surface area of up to 200 m^2 /g, which leads to formation of clusters due to van der Waals forces. The elastic modulus, strength and thermal properties of a composite are related to the volume fraction of the reinforcement added. Hence, a homogeneous distribution of reinforcement is essential as it translates into homogeneous properties of the composite. Clustering leads to concentration of reinforcement at certain points and this leads to worsening of overall mechanical properties.

[0006] Several methods have been developed to uniformly distribute the CNTs in metal matrixes. Excellent dispersion of CNTs in Al powders can be achieved by ball milling. Other methods grow CNTs on Al powders which are then used to fabricate composites by pressing and sintering. However, bringing this method to an industrial scale has not been realized yet. Ball milling leads to high volume outputs and excellent dispersion but might result in the damage to CNTs. In most of the dispersion methods the main effort is on creating a composite material with improved mechanical properties in comparison to the matrix metal. Only a few researchers have studied the effect of CNT in MMCs on electrical properties.

[0007] Because of the possible current carrying density of three orders of magnitude higher than Cu or Al, CNTs might also be used as enhancement of the electrical properties of metals. However, aluminum / CNT composites prepared by powder metallurgy display an increased electrical resistivity by more than 50%. A study by Yang et al. (Y. L. Yang, Y. D. Wang, Y. Ren, C. S. He, J. N. Deng, J. Nan, J. G. Chen and L. Zuo: Mater. Lett., 2008, 62, 47-50) showed at up to 10 wt-% SWCNT addition, that the electrical resistivity of Cu-CNT composites remains same as that of pure Cu. Feng et al. (Y. Feng, H. L. Yuan and M. Zhang: Mater. Charact., 2005, 55, 211-218) for Ag-CNT composites also showed a marginal increase in the electrical resistivity at up to 10 vol.-%CNT addition. The bad electrical property is attributed to the increase in interfacial area, the formation of insulating interface layers like Al_2O_3 and Al_4C_3, and strain in the matrix due to presence of CNT clusters, both of which hinders electron transfer through the composite (source: Bakshi et al. Carbon nanotube reinforced metal matrix composites, International Materials Reviews 2010 VOL 55 NO 1).

[0008] For making efficient electrical power cables it is therefore desirable to create a highly conductive metal / CNT structure wherein oxide and/or carbide layers do not hinder the flow of electrical current through the structure and which still has at least the mechanical performance of the pure metal matrix metal.

[0009] CN101948988 (A) discloses a method for manufacturing a CNT (carbon nanotube) composite transmission conductor by performing the following steps:

[0010] 1. filling MWCNTs (multiwalled carbon nanotubes) into holes uniformly drilled into an aluminum block, so that up to 7% of the total mass of the filled block consist of MWCNTs;

[0011] 2. stacking two aluminum blocks into which the MWCNTs powder have been filled inversely using a blind-hole method;

[0012] 3. extruding the stacked block in order to prepare a composite material rod;

[0013] 4. tandem rolling of the rod;

[0014] 5. drawing of the rolled composite material into a round wire shape;

[0015] 6. stranding the round wires by a wire twisting machine;

[0016] 7. feeding the twisted wire through a back-twisting stress eliminating device to obtain a single-stranded CNT composite cable.

[0017] Although this method provides for good electrical current flow through the MWCNT channels there is still the problem of the current transfer through the electrical interface between the MWCNTs and the aluminum matrix which leads to a still high electrical resistance of the cables produced in the described way. Also, the manufacturing process is rather complicated resulting in high manufacturing cost.

[0018] It is therefore desirable to create a method wherein the electrical interface between the CNTs and the metal matrix is optimized and which can be realized in a low number of production steps.

[0019] Recently several methods have been disclosed to get CNTs in good electrical contact with metal surfaces.

[0020] JP2007157372 (A) discloses a method wherein a copper or aluminum wire is coated with a plating liquid which is made by mixing CNTs in a molten salt made by mixing and melting 20 to 80 mol% aluminumhalide, 80 to 20 mol% 1, 3-dialkylimidazolium halide (provided that the carbonnumber of an alkyl group is 1 to 12), and monoalkylpyridinium halide (provided that the carbonnumber of an alkyl group is 1 to 12).

[0021] JP2009287112 (A) discloses a method wherein an iron, copper, or aluminum wire is coated with CNTs by using gold as the CNT carrier and interface material.

[0022] Although the last two methods provide a good electrical interface between the CNTs and the metal core material the manufacturing cost are high and the electrical current density capacity is limited due to the limited thickness of the coatings.

Disclosure of the invention

Technical problem

[0023]

Solution to problem

Technical Solution

[0024] Recently several methods have been disclosed to grow CNTs directly on a metal surface.

[0025] KR100827951 (B1) discloses a method for growing CNTs directly on the surface of a nickel foil. However. the catalyst particles sitting on the nickel surface, and where the CNTs start growing on, act as a current limiting layer between the CNT and the nickel substrate.

[0026] WO 2008/105809 A2 discloses a method for carbon nanotube growth on a metallic substrate using vapor phase catalyst delivery. This eliminates the current limiting catalyst layer between the substrate and the CNT.

[0027] The present invention uses a metal foil with a directly grown-on CNT carpet, which has been grown on the foil for instance by using the method disclosed in WO 2008/105809 A2. The foil is then rolled so that a tube or rod is created with a circular structure of alternating metal and CNT layers (Figure 1). The circular structure is then compacted in a metal rolling press, creating a flat metal sheet wherein the CNT layers are directly interconnected. The resulting sheet is then rolled-up again to form a new tube or rod similar to that depicted in Figure 1 but with much thinner layers. The compacting and rolling processes can be repeated several times leading to a multitude of thin CNT layers in an aluminum tube or rod which are all interconnected.

[0028] In a final step the resulting layered sheet is rolled to form a rod which is then drawn to shape in a wire draw machine to form an electrical wire with the desired diameter. Since all CNTs in the rod are connected on one side directly with the metal substrate where they were grown on, the electrical resistance between the metal and the CNTs is very low and the layered structure provides for high current density capacity.

[0029] In another embodiment of the invention the metal foil with the grown-on CNTs can also be wrapped around a metal- or non metallic composite material core where the core provides for the mechanical strength of the cable (Figure 2).

[0030] In another embodiment of the invention the metal foil with the grown-on CNTs can be folded in a mold in a random way to form a structure similar to a labyrinth (Figure 3) which is then compacted in a linear press to form a solid composite body. This body is then rolled in a rolling press to form a sheet wich can be further processed as described above.

Advantageous effects of invention

Advantageous Effects

[0031] Since all CNTs are grown directly from the metal surface the electrical resistance between the CNTs and the metal substrate is extremely low. Since the CNT carpet is compressed during the press rolling processing, the CNTs entangle and form a dense and highly conductive CNT network between the metal layers. Because of the high current density capacity of the CNTs the resulting composite cable has a higher current density capacity than the pure metal alloy. Because of the low specific weight of the CNTs the composite cable has a lower weight than a cable made from the pure substrate metal alloy with the same diameter.

Brief description of drawings

Description of Drawings

[0032] Figure 1 shows a sheet metal substrate (dark layer) with a directly grown-on CNT carpet (grey layer), which is rolled to form a layered tube.

[0033] Figure 2 shows a sheet metal substrate with grown-on CNTs wrapped around a tubular core.

[0034] Figure 3 shows a sheet metal substrate with grown-on CNTs folded in a random way.

Best mode for carrying out the invention

[0035]

Mode(s) for carrying out the invention

[0036]

Industrial applicability

Industrial Applicability

[0037] The cables made according to the methods disclosed in the present invention are used for high power, low loss and low weight cable applications with high current density capacity.

Sequence listing free text

[0038]

Claims

1. Method for making an electrical cable with improved electrical conductivity by rolling a sheet metal substrate with directly grown-on carbon nanotubes, forming a layered tube or rod, and subsequent compacting, re-rolling of the resulting sheet to form a rod and final drawing that rod to the desired cable diameter.
2. Method for making an electrical cable with improved electrical conductivity by rolling a sheet metal substrate with directly grown-on carbon nanotubes, forming a layered tube or rod, and subsequent compacting, and wrapping the resulting layered sheet around a metal or composite core.
3. Method for making an electrical cable with improved electrical conductivity by rolling a sheet metal substrate with directly grown-on carbon nanotubes, forming a layered tube or rod, and subsequent compacting, folding the resulting layered sheet in a mold in a random way, compacting the resulting randomly layered structure to form a sheet metal which is rolled to form a rod, and finally drawing that rod to the desired cable diameter.

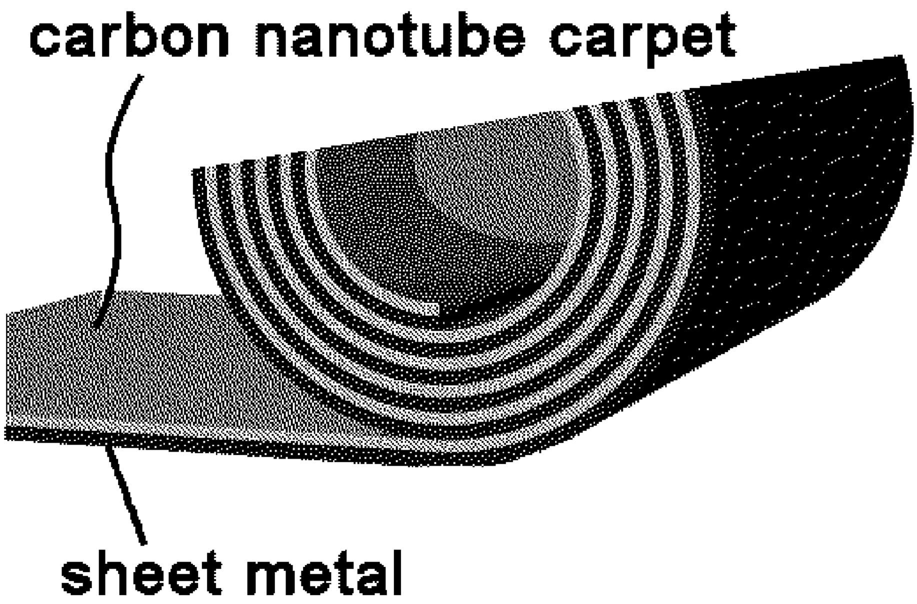
carbon nanotube carpet
sheet metal

Fig. 1

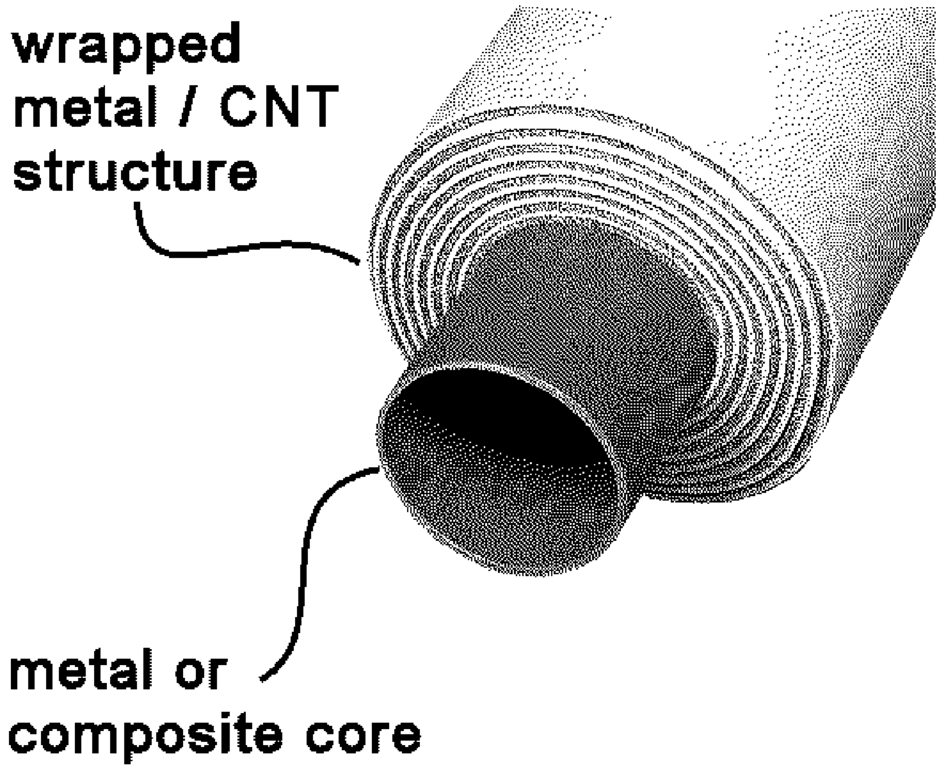
wrapped
metal / CNT
structure
metal or
composite core

Fig. 2

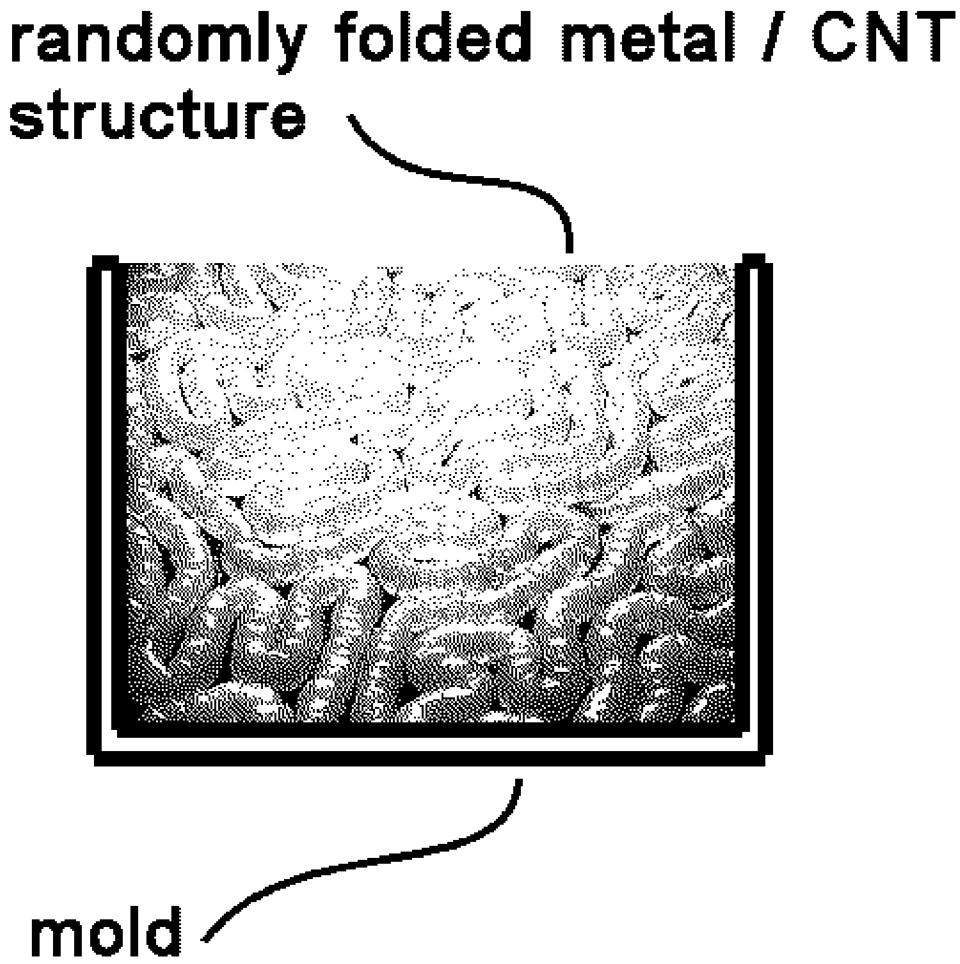

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/053385

A. CLASSIFICATION OF SUBJECT MATTER
INV. C22C47/20 C22C49/14 H01B1/02 H01B1/04 H01B7/00
B82Y30/00
ADD.

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)
C22C H01B B82Y

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2008/105809 A2 (RENSSELAER POLYTECH INST [US]; TALAPATRA SAIKAT [US]; KAR SWASTIK [US]) 4 September 2008 (2008-09-04) cited in the application paragraphs [0045], [0049]; claims 1-20	1-3
A	US 2005/238810 A1 (SCARINGE ROBERT P [US] ET AL) 27 October 2005 (2005-10-27) paragraph [0010] - paragraph [0020]; claims 1-52	1-3
A	US 2012/045644 A1 (WEI YANG [CN] ET AL) 23 February 2012 (2012-02-23) paragraph [0041] - paragraph [0045]; claims 1-19	1-3

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 January 2013	17/01/2013

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/053385

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2008105809 A2	04-09-2008	US 2012128880 A1 WO 2008105809 A2	24-05-2012 04-09-2008
US 2005238810 A1	27-10-2005	NONE	
US 2012045644 A1	23-02-2012	CN 102372253 A US 2012045644 A1	14-03-2012 23-02-2012