

A Method Of Producing Surface-Modified Carbon Nanotube And A Composite Containing The Same

Technical Field

5 The present disclosure relates a method of producing surface-modified carbon nanotube (CNT) and a product acquired thereof. More specifically, the surface-modified CNTs yielded in the disclosed method are at least partially assembled with metal and/or metal oxide particles on the elongate surface that the surface-modified CNTs can be homogeneously doped or blended into a liquid faction of a metal of similar or different type to form a
10 composite or alloy containing the surface-modified CNTs. Also, the present disclosure includes the formed metal composite being imparted with the desired physiochemical properties.

Background

15 Carbon nanotube (CNT) is a promising structured material exhibiting interesting optical, mechanical and electronic properties. It can come in the form of single-walled or multi-walled. Owing to the unique honeycomb arrangement and covalent sp^2 bond of the carbon atoms in the graphene layer, CNTs possess superb mechanical strength and good chemical stability. Its electrical conductivity can be varied according to the manner of the graphene
20 sheet being wrapped or folded. Incorporating or doping preferred amount of CNTs in a constituent material such as metal to produce composite of modified or preferred properties is common approach adopted in composite manufacturing. Though not entirely inert chemically, surface of CNT is substantially inactive. This can be attributed to mere intermolecular van der Waals interaction established at the basal plane of the graphene layer towards
25 surrounding molecules. Consequently, the composite containing the CNTs of inactive surface may yet to exert the desired properties in a full-fledged fashion. Numerous researches have been conducted in seeking effective way to active or functionalize surface of CNT, such that the interaction, at the basal plane, between the functionalized CNTs and the adjacent molecules is more of chemical bonding resulted by electrostatic force. For example, Japan
30 published patent no. 812310 teaches oxidation of CNTs using strong acids and the acid-treated CNTs show higher reactivity. Other oxidizing agents usable to functionalize CNTs are ozone, as proposed in Japan published patent no. 2003505332, and hydrogen peroxide, as

disclosed in Japan published patent no. 2004535349. China registered patent application no. 101311109 offers another method to create organic hard coating to the surface of CNTs by way of condensing alkoxide onto CNTs and subjecting the alkoxide-adhered CNTs to heat treatment until finally yielding the coating onto the surface of CNTs. Waki et al. also discuss ways to create pores on CNTs in United States patent publication no. 2011/0206932.

Most of the aforesaid methods no doubt impart the required changes to the surface of CNTs, but the modifications made may not be universally applicable for improving applications using or composites containing the modified CNTs. It is important that the incorporated modification is aligned to the downstream process using the modified CNTs. For instance, CNTs carrying surface hard coating or organic functional group is likely fail in significantly improving physiochemical properties of metal-based composite. Preferably, surface of the CNTs, which to be used for metal-based composite manufacturing, shall at least partially be lined or arranged with coating of metal particles. Zhang et al. discloses a method of producing CNTs with surface bearing metal particle in China patent publication no. 101830429 in which the disclosed method involves preparing blend of -COOH or -OH -functionalized CNTs and metal acetylacetonate in a tetrahydrofuran or chloroform followed by drying and heating the blend to finally give rise to metal-coated CNTs. In United States patent application no. 8227117, Hampden-Smith et al. also attempted to have metal catalysts supported onto CNTs by spray processing suspension having functionalized CNTs and active species of the metal to yield the catalysts. However, the metal-coated CNTs from the proposed methods of Zhang et al. and Hampden-Smith et al. can be undesirable for certain applications, such as alloy casting, due to presence of the hydrophilic functional group placed thereto for anchoring the metal particles. Also, the aforesaid method of Zhang et al. and Hampden-Smith et al. are far from environmental or user friendly considering the amount of flammable organic solvent and advanced machinery required respectively in their proposed methods. Thus, there exists a need to develop a simpler and less machine-dependent way to coat metal particles onto surface of CNTs

Summary

The present disclosure aims provide a method of producing surface-modified CNTs. Preferably, the modified surface of the CNTs is at least partially lined, coated or arranged with metal particles of desired property.

- 5 The present disclosure also offers a method of producing surface-modified CNTs, which possess coating or lining of metal particles on the modified surface, without creating chemical functional groups of the surface of the CNTs or functionalizing the surface of the CNTs using oxidative reagents or radicals. Forming functional groups on CNTs surface is generally undesirable partly down to oxygen carried in such functional, especially when the
10 produced modified CNTs is likely to be used for alloy casting.

Another object of the present disclosure is directed to offer surface-modified CNTs have surface area at least partially coated or lined with metal particles. The partially coated or lined metal particles of the present disclosure can function as effective means to prevent burning of
15 the modified CNTs when it is brought into contact with molten metal for the purpose of alloy casting.

More object of the present disclosure is pointed to a method of producing metal composite having surface-modified CNTs homogeneously dispersed in the matrix of the metal
20 composite. The surface-modified CNTs bear metal particles arranged at least on partial surface of the CNTs.

Still, an object of the present disclosure endeavors to create a metal composite or alloy using the aforesaid surface-modified CNTs, which are employed as a doping agent or modifier. The
25 disclosed composite can be produced from standard or conventional metal casting process through common metal casting furnace. The produced metal composite adaptably exhibits electrochemical or physiochemical properties substantially different from the casted metal block composed purely from the metal. More importantly, the disclosed composite or alloy requires only relatively small amount, around 0.01 to 0.5 by weight percentage, of the
30 aforesaid surface-modified CNTs for attaining the improved electrochemical or physiochemical properties. Such low required amount can be associated with resistance

imparted to the employed surface modified CNTs against burning in the alloy casting process, that less surface-modified CNTs will be burnt and wasted.

At least part or all the setting forth objects are met through one or more embodiments of the present disclosures that, in a number of embodiments, the present disclosure includes a method of producing surface-modified carbon nanotube comprising impregnating pre-treated carbon nanotubes with salt of a first metal in an aqueous portion to form a liquid suspension; removing the aqueous portion from the liquid suspension to yield salts of first metal-impregnated carbon nanotubes; and performing a first calcination of the salts of first metal-impregnated carbon nanotubes to produce a first surface-modified carbon nanotubes having surface modified or attached with oxide of the first metal. Preferably, the pre-treated carbon nanotubes are acquired by way of treating carbon nanotubes with acid and washing the treated carbon nanotubes with water.

In further embodiments, the disclosed method of surface-modified CNTs production may comprise the step of performing a second calcination of the first surface-modified carbon nanotubes in the presence of a reducing agent to yield a second surface-modified carbon nanotubes having surface modified or attached with nanoparticle of the first metal. Preferably, the reducing agent is in gas phase.

In a few embodiments of the disclosed method resulting in the first and/or second surface-modified carbon nanotubes, the first and/or second calcination is performed under inert gas flow at a temperature of 550 – 650 °C.

In accordance with more embodiments, the first metal used in the disclosed method of surface-modified carbon nanotube production can be aluminum, silver, iron, cobalt, copper, nickel, zinc, tin, chromium, molybdenum or tungsten.

Preferably, the salt of the first metal is in the form of nitrate, acetate or bicarbonate when the salts are employed in the disclosed method. More preferably, the salts of the first metal can be of other forms besides nitrate or bicarbonate as long the salts shows good solubility in an aqueous solution.

For some of the embodiments, the removal of the aqueous portion is performed by vaporizing the aqueous portion under heat treatment and/or reduced atmospheric pressure.

5 Another aspect of the present disclosure refers to a surface-modified carbon nanotube, preferably the second surface-modified carbon nanotubes, produced from the abovementioned method. For several embodiments, the surface-modified carbon nanotube comprises a carbon nanotube, having a diameter to length ratio of 10 to 1000, with nanoparticles of a first metal impregnated onto or arranged along part of its length by
10 impregnating the carbon nanotube with salt of the first metal in an aqueous portion to form a liquid suspension, removing the aqueous portion from the liquid suspension to yield salts of first metal-impregnated carbon nanotubes, performing a first calcination and a second calcination after the first calcination to the salts of first metal-impregnated carbon nanotubes to produce the surface-modified carbon nanotubes having surface modified or attached with
15 nanoparticle of the first metal. Preferably, the second calcination is performed in the presence of a gaseous reducing agent. The surface of the carbon nanotube is free from any chemical functional group preformed prior to the first calcination to react with the first metal.

For a number of embodiments of the disclosed surface-modified carbon nanotubes, the first
20 metal is preferably aluminum, silver, iron, cobalt, copper, nickel, zinc, tin, chromium, molybdenum or tungsten.

Further aspect of the present disclosure involves production of a composite or alloy containing the surface-modified carbon nanotube yielded from the aforesaid method that the
25 used surface modified carbon nanotube is free from being functionalize with hydrophilic chemical functional group for attachment or anchorage of the metal particles onto the surface of the carbon nanotube. Particularly, the disclosed method of producing the composite comprises the steps of impregnating pre-treated carbon nanotubes with salt of a first metal in an aqueous portion to form a liquid suspension; removing the aqueous portion from the liquid
30 suspension to yield salts of first metal-impregnated carbon nanotubes; performing a first calcination of the salts of first metal-impregnated carbon nanotubes to produce a first surface-modified carbon nanotubes having surface modified or attached with oxide of the first metal;

performing a second calcination to the first surface-modified carbon nanotubes in the presence of a gaseous reducing agent to produce a second surface-modified carbon nanotubes having surface modified or attached with nanoparticle of the first metal; mixing the produced second surface-modified carbon nanotubes with powder of a first metal to form a first mixture; activating the first mixture mechanically; introducing the mechanically activated first mixture into a molten fraction of a second metal in a homogeneous manner at a predetermined temperature to form a second mixture; and solidifying the second mixture to form the composite or alloy. Preferably, the first metal and/or second metal in the composite producing method is aluminum, silver, iron, cobalt, copper, nickel, zinc, tin, chromium, molybdenum or tungsten. The first metal is in the form of nitrate, acetate, or bicarbonate for composing the liquid suspension together with the pre-treated carbon nanotube.

In a number of embodiments, the first and second metals are different in the disclosed method. More preferably, first metal has melting point relatively higher than the second metal.

In a few embodiments, the first metal has melting point above or higher than the predetermined temperature.

Preferably, the first metal and the second surface-modified carbon nanotube are in a weight ratio of 0.1 to 1 for the composite acquired via the disclosed method.

In a number of embodiments, the composite producing method as disclosed herein further filters the molten fraction of the second metal, preferably before and after bringing the mechanically activated first mixture, using ceramic foam filters.

According to several embodiments of the composite producing method, the activating step is performed through ball milling

Still, another aspect of the present disclosure is about a composite comprising a first metal; a second metal; and a plurality of surface-modified carbon nanotubes being dispersed in a substantially homogeneous manner within the matrix of a second metal. Preferably, the carbon nanotubes are of a diameter to length ratio of 10 to 1000 with particles of a first

metal impregnated onto or arranged along part of its length by impregnating carbon nanotubes with salt of the first metal in an aqueous portion to form a liquid suspension, removing the aqueous portion from the liquid suspension to yield salts of first metal-impregnated carbon nanotubes, and performing a first calcination and a second calcination after the first calcination to the salts of first metal-impregnated carbon nanotubes to produce the surface-modified carbon nanotubes having surface modified or attached with nanoparticle of the first metal. Accordingly, the second calcination is performed in the presence of a gas phase reducing agent. Also, the plurality of surface-modified carbon nanotubes are mixed with the first metal in powder forming a first mixture being mixed and dispersed in the matrix of a molten fraction of the second metal. The surface of the carbon nanotube is free from any chemical functional group preformed prior to first calcination to react with the first metal. The surface of the carbon nanotube is free from any chemical functional group preformed prior to first calcination to react with the first metal.

In some embodiments of the composite, the first metal and second metal are different. Still, the first metal and the second metal are the same in other embodiments of the composite.

For a plurality of the preferred embodiments, the first mixture is mechanically activated prior to being dispersed in a molten fraction of the second metal. Likewise, the first metal is aluminum, silver, iron, cobalt, copper, nickel, zinc, tin, chromium, molybdenum or tungsten.

More embodiments of the disclosed composite contain carbon nanotubes of 0.01 to 0.1% by weight percentage of the composite.

Brief Description of Drawings

Figure 1 is an electron micrograph showing one embodiment of the surface-modified CNTs acquired through the present disclosure that element 1 refers to CNT and element 2 denotes nanoparticles of a metal attached to the surface of the CNTs; and

Figure 2 shows one possible establishment of the casting mold to bring the surface-modified CNTs into contact with the molten metal fraction to create the composite, with (a) illustrating top view of the casting mold and (b) depicting cross-sectional side view of the casting mold.

5

Detailed Description

The present invention may be embodied in other specific forms without departing from its structures, methods, or other essential characteristics as broadly described herein and claimed hereinafter. The described embodiments are to be considered in all respects only as
10 illustrative, and not restrictive. The scope of the invention is, therefore, indicated by the appended claims, rather than by the foregoing description. All changes that come within the meaning and range of equivalency of the claims are to be embraced within their scope.

According to one aspect of the present disclosure, a method of producing surface-modified
15 CNTs is disclosed. Essentially, the method comprises the steps of impregnating pre-treated carbon nanotubes with salt of a first metal in an aqueous portion to form a liquid suspension; removing the aqueous portion from the liquid suspension to yield salts of first metal-impregnated carbon nanotubes; and performing a first calcination of the salts of first metal-impregnated carbon nanotubes to produce a first surface-modified carbon nanotubes having
20 surface modified or attached with oxide of the first metal.

Before impregnating the CNTs with salt of the first metal, the CNTs are preferably subjected to pretreatment such as cleaning, drying or other dimensional modification before being brought into contact with the salts of the first metal dissolved in an aqueous portion.
25 Preferably, the pretreatment may include cleaning surface of the CNTs with mild acidic solution of, but not limited to, nitric acid. Other acids applicable for the cleaning step are any one or combination of sulfuric acid, hydrochloric acid and nitric acid. The acidic solution for cleaning surface of the CNTs is preferably in a pH range of 1 to 4. Following cleaning of the CNTs surface, acidic residues remained on the CNTs surface are removed by washing the
30 cleaned CNTs with water, preferably ionized water, until the washed surface reaches substantially neutral in pH. The CNTs are rid of moisture or humid after the cleaning and washing steps. Preferably, the disclosed method heat the washed CNTs at a temperature

around 90 to 100 °C vaporize the moisture collected to the CNTs. The surface of CNTs is not substantially functionalized, rendered active or enhanced with chemical reactivity via the pretreatments of any form in the present disclosure.

- 5 The pretreatment is further succeeded with the step to impregnate the pre-treated CNTs with salt of the first metal. The salt is preferably dissolved in an aqueous portion in order to reacting with the pre-treated CNTs. The pre-treated CNTs are mixed, preferably in a homogenous fashion, in the salted aqueous portion containing metal to be attached, anchored, adhered or embedded onto the surface of the CNT to form a liquid or aqueous suspension.
- 10 The formation of the liquid suspension having the CNTs and salts of the first metal can be obtained by stirring the mixture constantly for 30 to 60 minutes using any stirring tool or means known in the field. More preferably, the salt of the first metal and the CNTs are in a molar ratio of 0.15 to 1.5 in the liquid suspension. The acquired liquid suspension then proceeds to the step or process for removing the aqueous portion. In more specific, the
- 15 disclosed method vaporizes the aqueous portion into steam or water vapor off the liquid suspension. Removal of the aqueous portion can be attained by way of heating the liquid suspension, optionally under reduced atmospheric pressure to expedite the rate of vaporization. It is possible to rid the liquid suspension of the aqueous portion through centrifugation under reduced atmospheric pressure also. Upon removing the aqueous portion
- 20 completely, the disclosed method concentrates the suspended CNTs and salt of the first metal to finally yield powdery residues. These powdery residues are the salts of first metal-impregnated carbon nanotubes, which is an intermediate product with salt of the first metal contacting or adhering to at least partial surface of the CNTs. These powdery residues may be further dried to eliminate moisture or humid introduced from the aqueous portion.
- 25 Subsequently, the salts of first metal-impregnated CNTs undergo the first calcination to produce first surface-modified CNTs. More specifically, the first calcination is conducted in a flow reactor by heating the salts of first metal-impregnated CNTs at a temperature of 550 – 650 °C for around 15 to 120 minutes that the salts of first metal-impregnated carbon
- 30 nanotubes become oxidized in the first calcination turning into the first surface modified-CNTs with surface modified or attached with oxide of the first metal. In some respects, the first surface modified-CNTs of the present disclosure can be considered as first metal oxide

of nano size supported on CNT-based platform. It is important to note that the first surface modified-CNTs produced thereof can be utilized for other applications like electrochemical catalysts in synthesis of various chemical compounds.

5 More preferably, the disclosed method proceeds to further performing a second calcination of the first surface-modified CNTs in the presence of a reducing agent to finally yield second surface-modified CNTs. The second surface modified-CNTs preferably have at least part of its surface modified or attached with nanoparticle of the first metal. More specifically, the first surface modified-CNTs have the metal oxide reduced into nanoparticles of the first metal
10 in concurrent heating at a temperature of 550 – 650 °C for around 15 to 120 minutes, with one or more reducing agent brought into contact with the first surface modified-CNTs. For some embodiments, the reducing agent is a gas phase being pumped into the flow reactor and flowing by surface of the first surface modified-CNTs to continuously reduce the metal oxide while the side products of the redox reaction are channeled out of the reactor following the
15 gas flow. Preferably, the gaseous reducing agent is introduced into the reactor together with a carrier gas such as hydrogen during the second calcination. The reducing agent can be methane, hydrogen, paraffin or any combination derived thereof.

In accordance with several embodiments of disclosed method, the first metal employed can
20 be aluminum, silver, iron, cobalt, copper, nickel, zinc, tin, chromium, molybdenum or tungsten. Further, salts of the first metal used in the present disclosure are of good solubility in the aqueous phase or portion such that the realization of the liquid suspension in the subsequent step is feasible. The salt of the first metal can be, but not limited to, in the form of nitrate acetate, or bicarbonate.

25 Also, one aspect of the present disclosure refers to surface-modified CNTs, preferably the aforementioned second surface-modified CNTs, having at least part of the elongate surface coated, lined, adhered, embedded or arranged with nanoparticles of the first metal. The elongate surface of the mentioned CNTs is free of any chemical function groups preformed
30 thereof before being brought into with first metal. The surface-modified CNTs described herein can be produced or acquired at least through the method or process setting out in the foregoing description. Particularly, the surface-modified CNT of the present disclosure

comprises a carbon nanotube, having a diameter to length ratio of 10 to 1000, with nanoparticles of a first metal impregnated onto or arranged along part of its length as illustrated in Figure 1. Moreover, the surface-modified CNTs in this aspect can be obtained by way of impregnating the carbon nanotube firstly with salt of the first metal in an aqueous portion to form a liquid suspension, removing the aqueous portion from the liquid suspension to yield salts of the first metal-impregnated carbon nanotubes, and performing a first calcination and a second calcination, which proceeds after the first calcination, to the salts of first metal-impregnated carbon nanotubes to finally produce the surface-modified carbon nanotubes having surface modified or attached with nanoparticle of the first metal. In the first calcination, the salts of the first metal are decomposed thermally into oxide of the first metal or first metal oxide clinging or anchoring onto the surface of the CNTs. As described in the foregoing, the second calcination is performed, but not limited to, in the presence of a gas phase reducing agent being directed to the react with first metal oxide under heat treatment. Upon contacting the metal oxide in a heated environment, the reducing agent spontaneously reduce the first metal oxide on the surface of the CNTs to become nanoparticles of the first metal. Hydrophilic chemical functional groups such as carboxylic acids or hydroxyl are generally taught in the field to be created or synthesized on the surface of the CNTs to functionalize the CNTs that these chemical functional groups serve as a means to join or bind metal particles to the CNTs' surface in subsequent reaction. In more preferable embodiments, the second calcination in the disclosed method substantially removes or reduces chemical functional groups, which are likely formed under heating of the first calcination. Presence of such chemical functional groups on the CNTs can be sometimes undesirable when the derived metal bound-CNTs are subsequently implemented for certain downstream processes like doping or filling for metal alloy casting. Particularly, these chemical functional groups possess oxygen and the like elements that electrochemical or physiochemical properties of the alloy produced thereof can be adversely affected by these elements. Further, existence of such chemical functional groups on the surface of the CNTs may render the functionalized CNTs more vulnerable to burning in the alloy casting process. It was found by inventors of the present disclosure that particles of the first metal can be alternatively impregnated or attached onto the surface of the CNTs, without substantially creating chemical functional group on the surface of the CNTs. More importantly, the second calcination performed in the present disclosure can significantly reduce or remove chemical functional groups

unintentionally generated in the prior steps. Therefore, the disclosed surface modified-CNTs of the present disclosure are substantially free from any chemical functional group.

5 Likewise, the first metal referred in the disclosed surface-modified CNTs can be aluminum, silver, iron, cobalt, copper, nickel, zinc, tin, chromium, molybdenum or tungsten.

Pursuant to another aspect of the present disclosure, a method of producing a composite or alloy doped or filled with the aforesaid surface modified-CNTs coated or adhered with nanoparticles of the first metal is described hereinafter in details. Accordingly, the method of
10 producing the composite comprises the steps of impregnating pre-treated carbon nanotubes with salt of a first metal in an aqueous portion to form a liquid suspension; removing the aqueous portion from the liquid suspension to yield salts of first metal-impregnated carbon nanotubes; performing a first calcination of the salts of first metal-impregnated carbon nanotubes produce a first surface-modified carbon nanotubes having surface modified or
15 attached with oxide of the first metal; performing a second calcination to the first surface-modified carbon nanotubes in the presence of a gaseous reducing agent to produce a second surface-modified carbon nanotubes having surface modified or attached with nanoparticle of the first metal; mixing the produced second surface-modified carbon nanotubes with powder of a first metal to form a first mixture; activating the first mixture mechanically; introducing
20 the mechanically activated first mixture into a molten fraction of a second metal, which is different from the first metal, in a homogeneous manner at a predetermined temperature to form a second mixture; and solidifying the second mixture to form the composite.

According to preferred several embodiments, the CNTs are preferably subjected to
25 pretreatment such as cleaning, drying or other dimensional modification before being brought into contact with the salts of the first metal dissolved in an aqueous portion. Preferably, the pretreatment may include cleaning surface of the CNTs with mild acidic solution of pH value ranged from 1 to 4. Acidic residues on the CNTs surface are then cleared by washing the CNTs with water until the washed CNTs become substantially neutral in pH. The CNTs can
30 be subjected to oven drying before impregnated with the salts of the first metals. The pretreatments conducted in the disclosed method for producing the composite or alloy are not intended to create or synthesize chemical functional groups onto surface of the CNTs as

opposed to some of the early disclosed techniques in the field. The surface of CNTs is not substantially functionalized, rendered active or enhanced with chemical reactivity via the pretreatments of any form according to preferred embodiments of the described method.

- 5 For the step of impregnating or contacting the pre-treated CNTs with salt of the first metal, the pre-treated CNTs are preferably added into an aqueous portion with the salt of the first metals dissolved therein. The pre-treated CNTs are mixed, preferably in a homogenous fashion, in the salted aqueous portion containing first metal to be attached, anchored, adhered or embedded onto the surface of the CNT to form a liquid or aqueous suspension. More
10 preferably, the salt of the first metal and the CNTs are in a molar ratio of 0.15 to 1.5 in the liquid suspension. The acquired liquid suspension then proceeds to the step or process for removing the aqueous portion. Removal of the aqueous portion can be attained by way of heating the liquid suspension, optionally under reduced atmospheric pressure. Alternatively, aqueous portion can be vaporized through centrifugation under reduced atmospheric pressure.
15 Vaporizing off the aqueous portion progressively concentrates the suspended CNTs and salt of the first metal to finally yield powdery residues. These powdery residues are the salts of first metal-impregnated carbon nanotubes, which is an intermediate product with salt of the first metal contacting or adhering to at least partial surface of the CNTs.
- 20 As stated above, the salts of first metal-impregnated CNTs undergo the first calcination in the disclosed method to produce first surface-modified CNTs. Preferably, the disclosed method has the first calcination conducted in a flow reactor by heating the salts of first metal-impregnated CNTs at a temperature of 550 – 650 °C for around 15 to 120 minutes that the salts of first metal-impregnated carbon nanotubes become oxidized in the first calcination
25 turning into the first surface modified-CNTs with surface modified or attached with oxide of the first metal. The disclosed method has the second calcination of the first surface-modified CNTs pursued succeeding to the first calcination. The second calcination preferably yields second surface-modified CNTs with the help of a reducing agent that the yielded second surface modified-CNTs preferably have at least part of its surface modified or attached with
30 nanoparticle of the first metal. More specifically, the first metal oxide on the first surface modified-CNTs is reduced into nanoparticles of the first metal by the reducing agent under concurrent heating at a temperature of 550 – 650 °C for around 15 to 120 minutes. The

reducing agent is preferably a gas phase being directed into the flow reactor and flowing by the surface of the first surface modified-CNTs to continuously reduce the metal oxide while the side products of the redox reaction are channeled out of the reactor in the gas flow. Preferably, the gaseous reducing agent is introduced into the reactor together with a carrier gas such as hydrogen during the second calcination. The reducing agent can be methane, hydrogen, paraffin or any combination derived thereof.

In order to have the second surface-modified CNTs filled or doped into the molten fraction of the second metal without substantially decomposed by the extreme heat, the disclosed method preferably prepares the second surface modified CNTs into the first mixture in which second surface-modified CNTs become substantially enclosed and mechanically activated. More specifically, the obtained second surface modified-CNTs are blended with powder or fine aggregates of the first metal forming the first mixture. The weight ratio of the second surface modified CNTs to the powder of the first metal in the first mixture is preferably 0.5-1.5: 2-6. Once the blending or mixing is completed, the disclosed method activates the first mixture mechanically by at least ball milling. The mechanical activation in the disclosed method ensures particle size of the powder or fine aggregates of the first metal in the first mixture is significantly reduced. Increased fineness in the powder of the first metal lead to diameter to length diameter to length improved available specific surface area of the first mixture that the mechanically activate first mixture is more readily to react with the molten fraction of the second metal in succeeding steps. The performed mechanical activation also promotes homogenous mixing of the particles and/or components. Optionally, the mechanically activated first mixture can be loosely packed or compressed into tablets or spheres to ease the handling.

Preferably, the composite or alloy acquired from the disclosed method can be produced by contacting the mechanically activated first mixture with the molten fraction of the second metal in a conventional or standard metal casting furnace 100 as illustrated in Figure 2. Particularly, the furnace has a vertically erected flow channel with two layers of ceramic foam filters 10, 30 positioned beneath an open top of the flow channel. The mechanically activated first mixture, preferably in the form of tablet or sphere, is placed within the flow channel and between the two layers of ceramic foam filters. Pouring the molten fraction of

the second metal via the open top of the furnace inevitable channels the molten fraction of the second metal through the paired filters and the first mixture sandwiched thereof. In short, the disclosed method filters the molten fraction of the second metal before and after introducing the mechanically activated first mixture into the molten fraction using ceramic foam filters.

5 The molten fraction flowing through filter gradually erodes away the first mixture positioned in the furnace thus slowly blending the first mixture, in which the second surfaced modified-CNTs are packed, into the molten fraction forming the second mixture. Preferably, the first mixture or at least the second surface modified-CNTs are blended into the molten fraction of the second metal in a homogeneous manner. The disclosed method shall subsequently have
10 the second mixture cast, extrude and/or solidifying to form the composite or alloy of desired.

Based upon a number of preferred embodiments, the second surface-modified carbon nanotubes are in an amount of 0.01 to 0.2 by weight percentage in the composite. It is important to note that the amount or weight percentage of the CNTs or the second surface-
15 modified CNTs in the produced composite or alloy is significantly lower than other similar products in the field. The non-chemical binding arrangement of the nanoparticles of the first metal on the surface of the CNTs, as in second surface modified-CNTs, and encapsulation of the acquired second surface modified-CNTs using mechanically activated powder of first metal have greatly improved resistance of the used CNTs against burning generally caused by
20 relatively high temperature of the molten fraction. In most of the known arts, it is almost impossible or unlikely to directly add, mix or blend CNT, with or without modifications, to the molten metal fraction for alloy production. Otherwise, great amount of CNTs has to be used to fill or dope into the molten fraction such that at least parts of the added CNTs potentially survive throughout the process without undergoing burning and finally impart the
25 desired properties into the formed alloy. However, such practice does not come easily without actual cost considering that significant amount of the added CNTs will be wasted. It is worth to note that raw CNTs is costly (present selling price is around USD1000-4000/kg). Cost to manufacture alloy in the expense of the used CNTs is high. Nevertheless, inventors of the present disclosure resolve the abovementioned hindrances in the field by way of firstly
30 yielding the second surface-modified CNTs and forming the mechanically activated first mixture using the yielded second surface-modified CNTs. Being enabled to place and mix the first mixture with the molten fraction of the second metal in the cast furnace or mold, the

disclosed method not only facilitates direct addition of the second surface-modified CNTs for alloy forming but also allows seamless integration of the described process into metal casting set up and flow currently employed in the field alloy production.

- 5 In accordance with preferred embodiments, the first metal and/or second metal used in the disclosed method can be aluminum, silver, iron, cobalt, copper, nickel, zinc, tin, chromium, molybdenum or tungsten. More preferably, the second metal is different from the first metal. Therefore, addition of the first metal, either coated on the second surface-modified CNTs or the metal powder in the first mixture, into the second metal leads to production of the desired
- 10 alloy. Apart from that, the first metal used in the disclosed method preferably has melting point above the predetermined temperature at which the molten fraction of the second metal is brought into contact with the first mixture. Higher melting point or temperature of the first metal than the molten fraction means the first metal in the first mixture retains its solid configuration when being mixed and engulfed by the molten fraction. The pulverized powder
- 15 and lined coating, in their solid state, surrounding or encapsulating the CNTs added to the molten fraction can somehow protect or shield the CNTs from potential burning in the process of mixing or doping the second metal. More specifically, the disclosed method prefers to have the first metal with melting point relatively higher than the second metal.
- 20 Further, salts of the first metal used in the present disclosure are of good solubility in the aqueous phase or portion such that the realization of the liquid suspension in the subsequent step is feasible. The salt of the first metal can be, but not limited to, in the form of nitrate acetate, or bicarbonate.
- 25 Another aspect of the present disclosure directs to a composite or alloy created from the aforementioned method requiring only relatively low amount of filling or doping CNTs, precisely the second surface modified-CNTs. The alloy or composite essentially comprises a first metal; a second metal; and a plurality of surface-modified carbon nanotubes being dispersed in a substantially homogeneous manner within the matrix of a second metal. The
- 30 plurality of surface-modified CNTs are of a diameter to length ratio of 10 to 1000 with particles of a first metal impregnated onto or arranged along part of its length by impregnating carbon nanotubes with salt of the first metal in an aqueous portion to form a

liquid suspension, removing the aqueous portion from the liquid suspension to yield first metal-impregnated carbon nanotubes, and performing a first calcination and a second calcination, which is after the first calcination, to the first metal-impregnated carbon nanotubes to produce the surface-modified carbon nanotubes having surface modified or attached with nanoparticle of the first metal. More importantly, the second calcination is performed in the presence of a gas phase reducing agent for reducing the oxide of the first metal generated in the first calcination into nanoparticles of the first metal arranged or adhered onto the surface of the CNTs. The surface of the carbon nanotube is free from any chemical functional group preformed prior to first calcination to react with the first metal.

To impart the produced alloy with the desired properties, the surface-modified carbon nanotubes are in an amount of 0.01 to 0.5 by weight percentage in the composite or alloy produce. It is important to note that there is an optimum amount of the described surface-modified CNTs, as modifier and/or doping reagents, implementable in the disclosed embodiments to improve the properties of the materials (alloys). This can at least partly attribute to the role of CNTs in providing centers of crystallization, such that it may foster degradation of the alloy properties when being presented in excess amount in the cast alloy.

Preferably, the plurality of surface-modified carbon nanotubes is mixed with the first metal in powder forming a first mixture being mixed and dispersed in the matrix of a molten fraction of the second metal. Particularly, the non-chemical binding arrangement of the nanoparticles of the first metal on the surface of the CNTs and enclosure or encapsulation of the acquired surface modified-CNTs using mechanically activated powder of first metal greatly facilitates incorporation of the prepared CNTs into the molten fraction of the second method to finally yield the alloy or composite of the present disclosure. More preferably, the first metal and second metal are different, with melting point of the first metal relatively higher than the second metal. Therefore, the first metal does not become molten when being added into the molten fraction of the second metal. For some embodiments, the first metal and/or second metal of the composite is aluminum, silver, iron, cobalt, copper, nickel, zinc, tin, chromium, molybdenum or tungsten.

The following example is intended to further illustrate the invention, without any intent for the invention to be limited to the specific embodiments described therein.

Example 1

5 10 g of single-walled carbon nanotubes (CNT) were added into "aqua regia" (100 ml) for pre-treatment and subjected to heating at a temperature of 100⁰C for 30 minutes with stirring using a magnetic stirrer. Then the CNTs were filtered and washed with distilled water to neutralize the acidic residues. Ore-treated CNTs were then poured into a solution of 10 g of silver nitrate in 100 ml of water to have the pre-treated CNTs suspended within the solution-
10 a liquid suspension. The liquid suspension was then subjected to heating under 90-100 ⁰C for removing the solution by vaporization. Upon removal of the solution, first intermediate compounds of "CNT- silver nitrate" were formed and further dried in air at 180 ⁰C on for 30 minutes. The dried first intermediate compounds were charged into a flow reactor and heated or calcinated in an inert atmosphere to a temperature of 600 ⁰C. for 30 min. The heating
15 resulted in formation of second intermediate compounds, CNT-Ag₂O. The CNT-Ag₂O compounds, especially the metal oxide particles, were subsequently reduced by methane in the presence of hydrogen gas flow to finally yield (10 litres per hour for CH₄ and 10 litres per hour of H₂) at a temperature of 600 ⁰C. for around 30 minutes Carbon nanotubes having surface modified with silver nanoparticles coating, embedment, anchorage, lining or
20 attachment (CNT-25% Ag) were finally created.

Carbon nanotubes with surface modified by silver in an amount of 3 g (2.4 g CNT- 0.6g Ag) were mixed with 12 g of metallic silver. The resulting mixture was subjected to mechanical activation in a planetary mill for 3 minutes. The mechanically-activated mixture was prepared
25 into a tablet of 30 mm diameter. The prepared tablet was weighted 15g per piece, with 3g of surface-modified CNTs and 12g of pure silver. One piece of the prepared tablet was placed between the ceramic foam filter through which a liquid or liquefied fraction of aluminium weighted 4.8 kg was filtered through and mixed with the prepared tablet as well as the surface-modified CNT disposed thereby to form a surface-modified CNTs-incorporated alloy
30 or composite. The resulting alloy contained silver of 0.26 and carbon of 0.05 by weight percentage. Tensile strength and strain at break of the produced alloy was then tested. Particularly, all tests were carried out in independent laboratory mechanical tests of samples,

materials and components of aviation equipment. Cylindrical samples were prepared for testing. Technical equipment for tests: a hydraulic test machine for testing under complex stress state, type BISS UTN-100kN, No. 100812610204.

5 Example 2

The processes of Example 1 were repeated in this experiment, except there were total 4 tablets being used to produce the alloy or composite. Each of the tablets was weighted 15g per piece, with 3g of surface-modified CNTs and 12g of pure silver.

10 Example 3

The processes of Example 1 were repeated in this experiment, except there were total 10 tablets being used to produce the alloy or composite. Each of the tablets was weighted 15g per piece, with 3g of surface-modified CNTs and 12g of pure silver.

15 Example 4

The processes of Example 1 were repeated in this experiment, except that the single-walled CNTs were replaced with multi-walled CNTs. Each of the tablets was weighted 15g per piece, with 3g of surface-modified CNTs and 12g of pure silver.

20 Example 5

The processes of Example 4 were repeated in this experiment, except there were total 4 tablets being used to produce the alloy or composite. Each of the tablets was weighted 15g per piece, with 3g of surface-modified CNTs and 12g of pure silver.

25 Example 6

The processes of Example 4 were repeated in this experiment, except there were total 10 tablets being used to produce the alloy or composite. Each of the tablets was weighted 15g per piece, with 3g of surface-modified CNTs and 12g of pure silver.

30 EXAMPLE 7

A metal article purely made of aluminium weighted 4.8 kg was used in this experiment as a negative control. Tensile strength and strain at break of the produced aluminium article was then tested.

- 5 Properties of the alloy or composite produced in Example 1 to 7 are compared in Table 1 below.

Example	Number of tablet and the type of CNTs used	Tensile strength (peak value) MPa	The strain at break (elongation),%
1	1 tablet with single-walled CNTs	71,76	30,62
2	4 tablets with single-walled CNTs	65,99	18,22
3	10 tablets with single-walled CNTs	56,72	12,12
4	1 tablet with multi-walled CNTs	62,73	16,53
5	4 tablet with multi-walled CNTs	56,14	13,36
6	10 tablet with multi-walled CNTs	48,67	9,33
7	Control composed purely of aluminium	37,99	5,08

Table 1

- 10 Although this invention has been described in its preferred form with a degree of particularity, it is understood that the present disclosure of the preferred form has been made only by way of example and that numerous changes in the details of construction and the combination and arrangements of parts may be resorted to without departing from the scope of the invention.

Claims

1. A method of producing surface-modified carbon nanotube comprising the steps of:
impregnating pre-treated carbon nanotubes with salt of a first metal in an
5 aqueous portion to form a liquid suspension;
removing the aqueous portion from the liquid suspension to yield salts of first
metal-impregnated carbon nanotubes; and
performing a first calcination of the salts of the first metal-impregnated carbon
nanotubes to produce a first surface-modified carbon nanotubes having surface
10 modified or attached with oxide of the first metal.
2. The method of claim 1 further comprising performing a second calcination of the first
surface-modified carbon nanotubes in the presence of a reducing agent to yield a
second surface-modified carbon nanotube having surface modified or attached with
15 nanoparticle of the first metal.
3. The method of claim 2, wherein the reducing agent is in gas phase.
4. The method of claim 1, wherein the first metal is aluminum, silver, iron, cobalt,
20 copper, nickel, zinc, tin, chromium, molybdenum or tungsten.
5. The method of claim 1, wherein the salt of the first metal is in the form of nitrate
acetate, or bicarbonate.
- 25 6. The method of claim 1, wherein the pre-treated carbon nanotubes are acquired by way
of treating carbon nanotubes with acid and washing the treated carbon nanotubes with
water.
7. The method of claim 1, wherein the removing step is performed by vaporizing the
30 aqueous portion under heat treatment and/or reduced atmospheric pressure.

8. The method of claim 1, wherein the first and/or second calcination is performed under inert gas flow at a temperature of 550 – 650 °C.

9. A surface-modified carbon nanotube comprising

5 a carbon nanotube, having a diameter to length ratio of 10 to 1000, with nanoparticles of a first metal impregnated onto or arranged along part of its length by impregnating the carbon nanotube with salt of the first metal in an aqueous portion to form a liquid suspension, removing the aqueous portion from the liquid suspension to yield salts of the first metal-impregnated carbon nanotubes, and performing a first
10 calcination and a second calcination after the first calcination to the salts of first metal-impregnated carbon nanotubes to produce the surface-modified carbon nanotubes having surface modified or attached with nanoparticle of the first metal,

 wherein the second calcination is performed in the presence of a gas phase reducing agent;

15 wherein the surface of the carbon nanotube is free from any chemical functional group preformed prior to first calcination to react with the first metal.

10. The surface modified carbon nanotube of claim 9, wherein the first metal is aluminum, silver, iron, cobalt, copper, nickel, zinc, tin, chromium, molybdenum or tungsten.

20

11. A method of producing a composite comprising the steps of:

 impregnating pre-treated carbon nanotubes with salt of a first metal in an aqueous portion to form a liquid suspension;

 removing the aqueous portion from the liquid suspension to yield salts of first
25 metal-impregnated carbon nanotubes;

 performing a first calcination of the salts of first metal-impregnated carbon nanotubes produce a first surface-modified carbon nanotubes having surface modified or attached with oxide of the first metal;

 performing a second calcination to the first surface-modified carbon
30 nanotubes in the presence of a gaseous reducing agent to produce a second surface-modified carbon nanotubes having surface modified or attached with nanoparticle of the first metal;

mixing the produced second surface-modified carbon nanotubes with powder of a first metal to form a first mixture;

activating the first mixture mechanically;

introducing the mechanically activated first mixture into a molten fraction of a second metal, which is different from the first metal, in a homogeneous manner at a predetermined temperature to form a second mixture; and

solidifying the second mixture to form the composite.

12. The method of claim 11 further comprising filtering the molten fraction of the second metal using ceramic foam filters before and after introducing the mechanically activated first mixture into the molten fraction.

13. The method of claim 11, wherein the first metal and/or second metal is aluminum, silver, iron, cobalt, copper, nickel, zinc, tin, chromium, molybdenum or tungsten.

14. The method of claim 11, wherein the first metal has melting point above the predetermined temperature.

15. The method of claim 11, wherein the first metal has melting point relatively higher than the second metal.

16. The method of claim 11, wherein the salt of the first metal is in the form of nitrate acetate, or bicarbonate.

17. The method of claim 11, wherein the pre-treated carbon nanotubes are acquired by way of treating carbon nanotubes with acid and washing the treated carbon nanotubes with water.

18. The method of claim 11, wherein the removing step is performed by vaporizing the aqueous portion under heat treatment and/or reduced atmospheric pressure.

19. The method of claim 11, wherein the calcinating step is performed under inert gas flow at a temperature of 550 – 650 °C.

20. The method of claim 11, wherein the activating step is through ball milling.

21. The method of claim 11, wherein the second surface-modified carbon nanotubes are
5 in an amount of 0.01 to 0.2 by weight percentage in the composite.

22. A composite comprising

a first metal;

a second metal; and

10 a plurality of surface-modified carbon nanotubes being dispersed in a substantially homogeneous manner within the matrix of a second metal, wherein the carbon nanotubes are of a diameter to length ratio of 10 to 1000 with particles of a first metal impregnated onto or arranged along part of its length by impregnating carbon nanotubes with salt of the first metal in an aqueous portion to form a liquid suspension, removing the aqueous
15 portion from the liquid suspension to yield first metal-impregnated carbon nanotubes, and performing a first calcination and a second calcination, which is after the first calcination, to the first metal-impregnated carbon nanotubes to produce the surface-modified carbon nanotubes having surface modified or attached with nanoparticle of the first metal,

20 wherein second calcination is performed in the presence of a gas phase reducing agent,

wherein the plurality of surface-modified carbon nanotubes is mixed with the first metal in powder forming a first mixture being mixed and dispersed in the matrix of a molten fraction of the second metal,

25 wherein the surface of the carbon nanotube is free from any chemical functional group preformed prior to first calcination to react with the first metal.

23. The composite of claim 22, wherein the first mixture is mechanically activated prior to being dispersed in a molten fraction of the second metal.

30 24. The composite of claim 22, wherein the first metal and/or second metal is aluminum, silver, iron, cobalt, copper, nickel, zinc, tin, chromium, molybdenum or tungsten.

25. The composite of claim 22, wherein the first metal and second metal are different.

26. The composite claim 22, wherein the surface-modified carbon nanotubes are in an amount of 0.01 to 0.1 by weight percentage in the composite.