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(54) **LAMINATE STRUCTURE**

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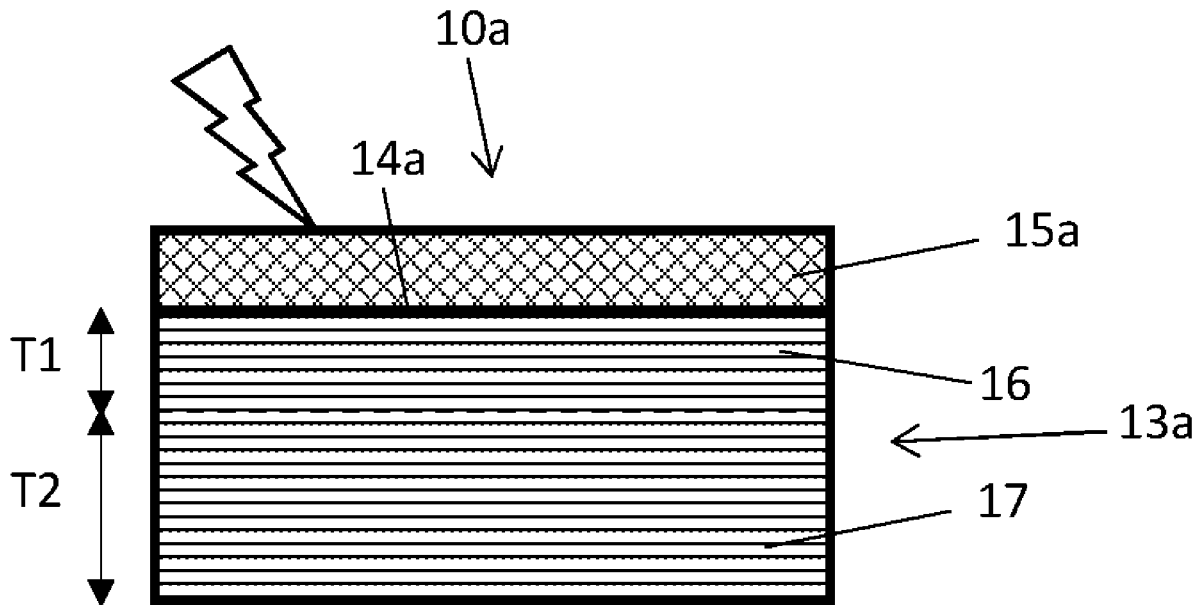
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(57) **ABSTRACT**

A laminate structure is disclosed including a fibre laminate impregnated with a laminate matrix material, and a veil of carbon nanotubes impregnated with a veil matrix material. The laminate matrix material and the veil matrix material doped with carbon particles. The veil provides lightning strike protection. The structure is manufactured by co-curing the laminate matrix material and the veil matrix material to bond the veil of carbon nanotubes to the fibre laminate.



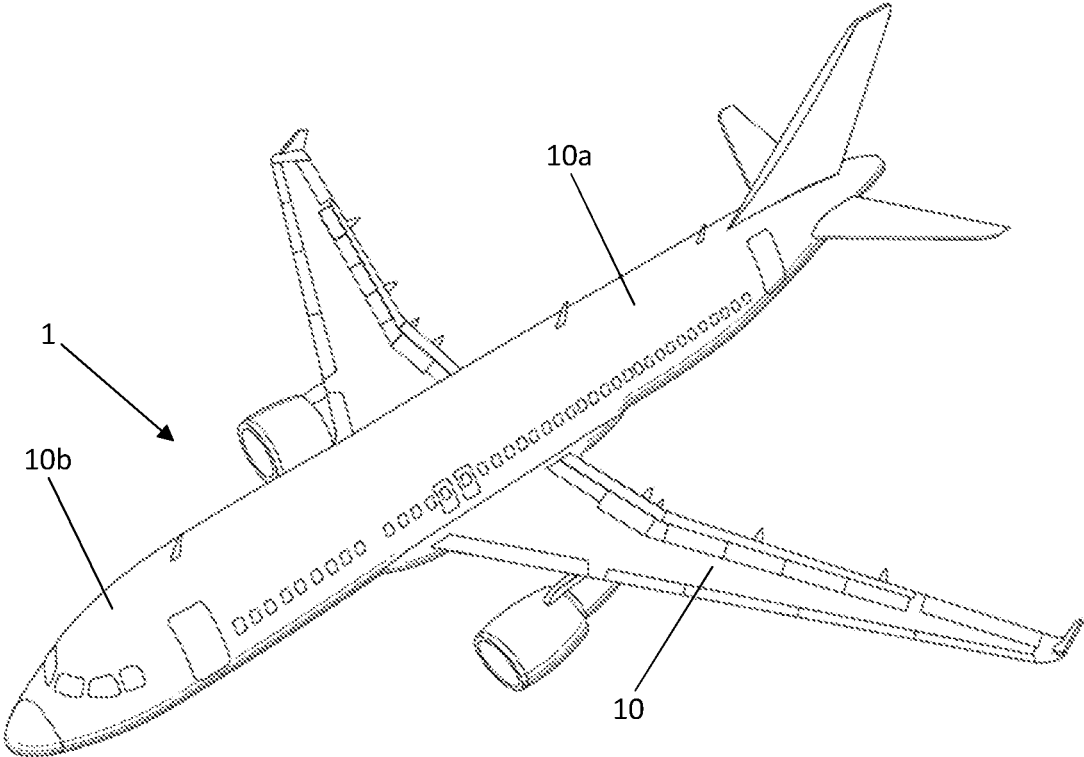


FIG. 1

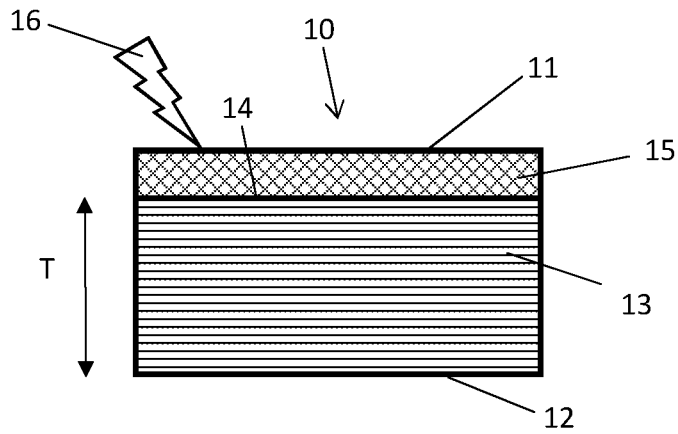


FIG. 2

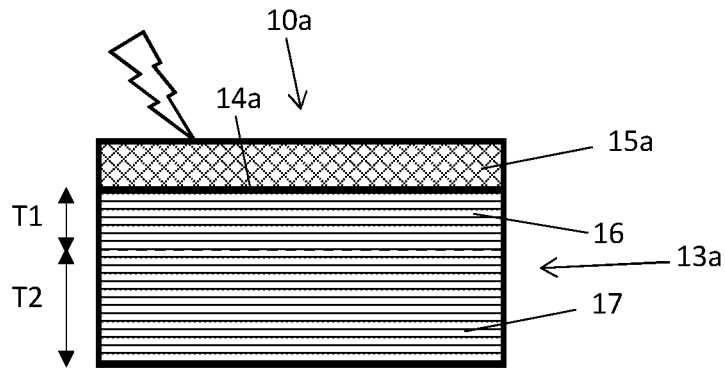


FIG. 3A

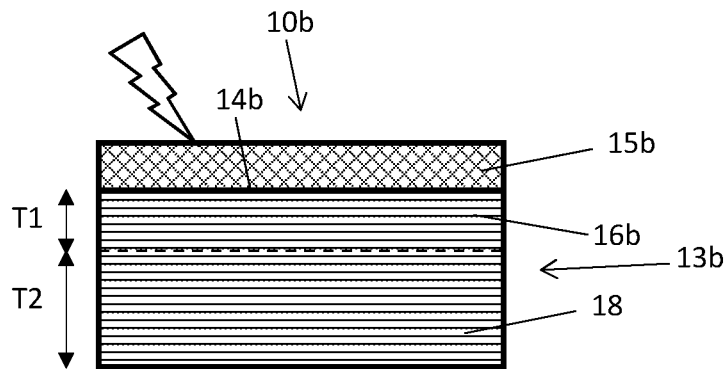


FIG. 3B

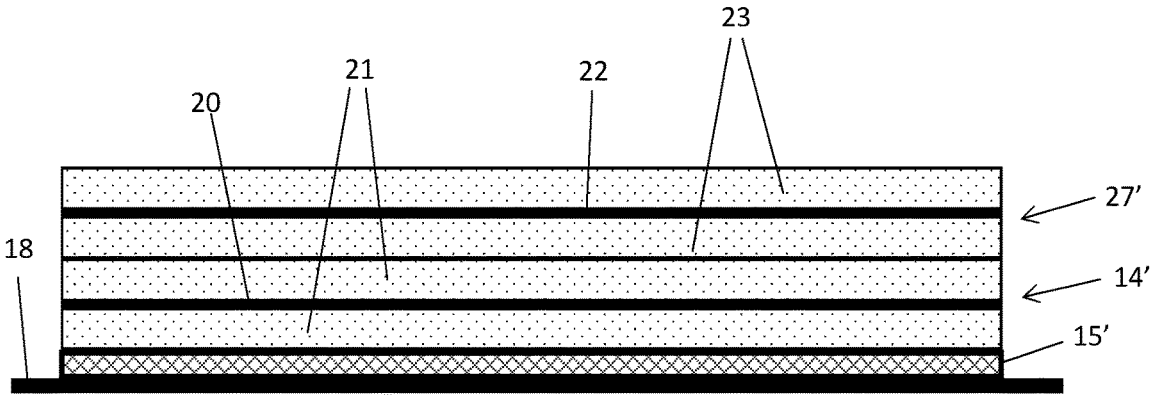


FIG. 4

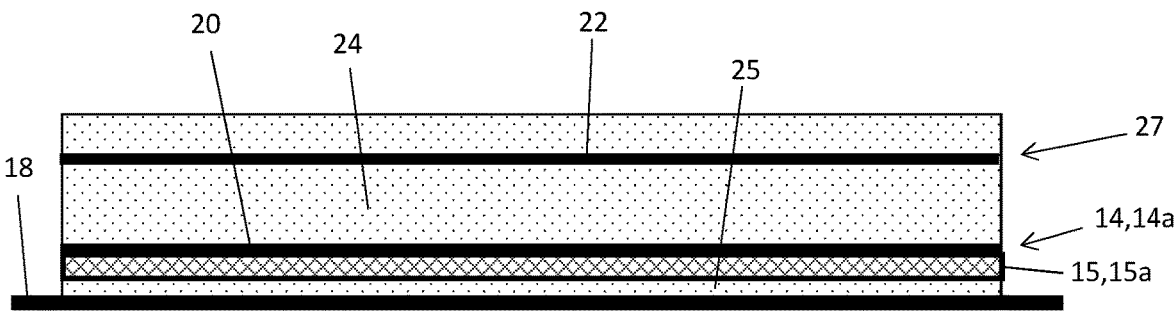
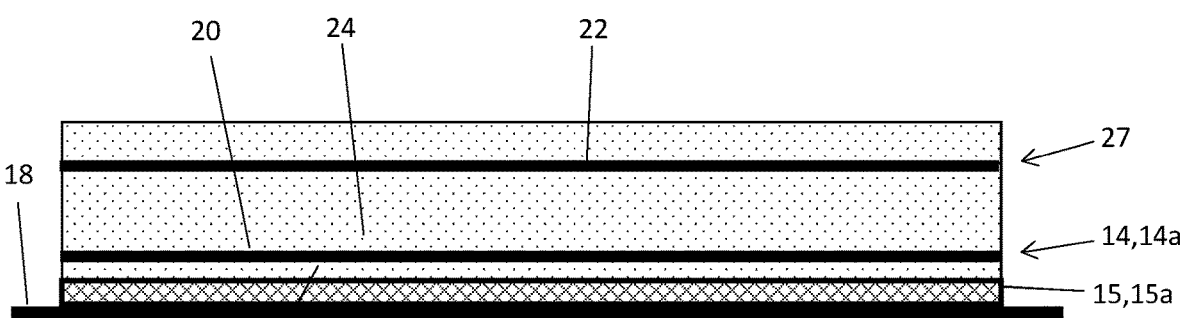


FIG. 5



26
FIG. 6

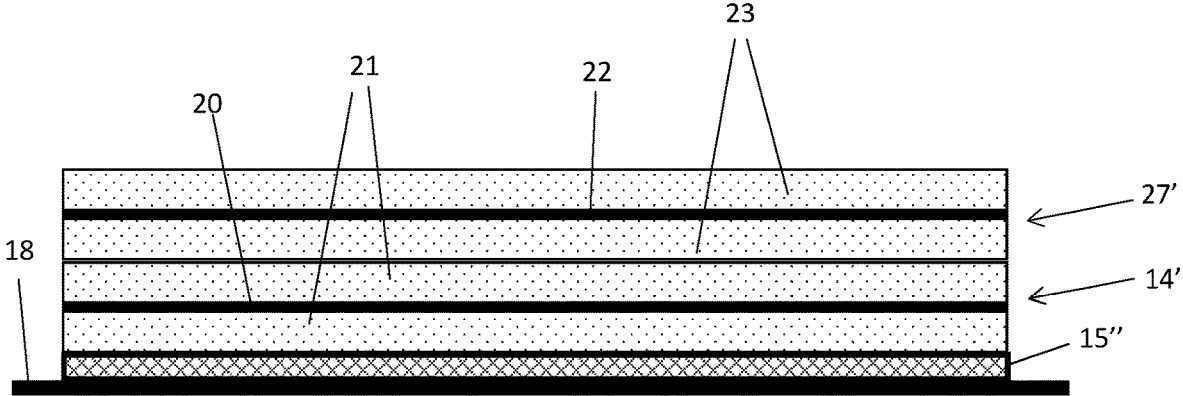


FIG. 7

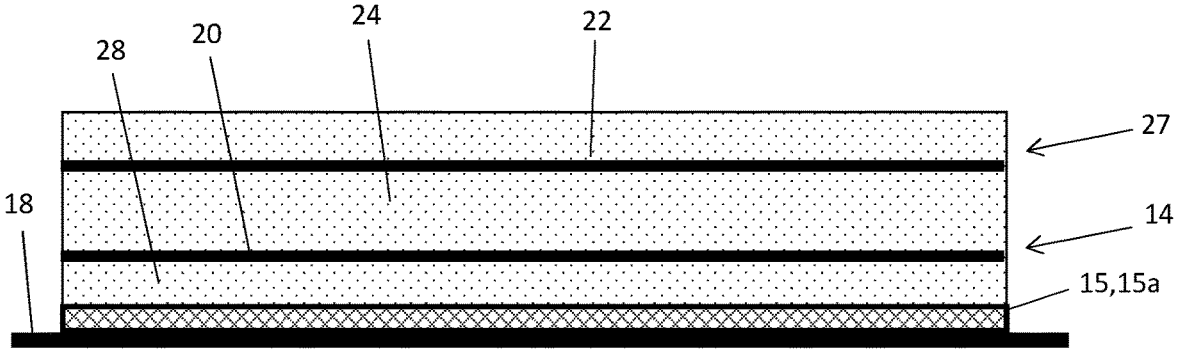


FIG. 8

LAMINATE STRUCTURE

FIELD OF THE INVENTION

[0001] The present invention relates to a laminate structure and a method of manufacturing a laminate structure. Typically, but not exclusively, the laminate structure is a part of an aircraft and is designed to protect the aircraft from lightning strike damage.

BACKGROUND OF THE INVENTION

[0002] Aircraft lightning strikes are frequent occurrences and can generate high forces and temperatures, which may cause structural damage and systems disruption.

[0003] Embedding metals in the carbon fibre reinforced polymer (CFRP) structure is a known protection method: the metal foil disperses the localised high energy of the lightning, reducing the structural damage and avoiding secondary effects that might compromise aircraft safety.

[0004] Work done since 2011-13 and published, among others, by Reference 1 (Yang et al) and Reference 2 (Tang et al), suggests that combining different carbon allotropes will enhance the in-plane and through-thickness electrical conductivity of CFRP laminates. A synergistic effect, resulting from mixing different carbon allotropes, is explained by Reference 3 (Karch et al, 2016). According to Reference 3, some studies have reported that simultaneous use of a mixture of CNTs and graphene platelets shows a synergistic effect between graphene platelets and MWCNTs. However, Reference 3 states that the effective electrical conductivity is still not sufficient for an application as a standalone lightning protection measure.

[0005] In Reference 4 (Karch et al, 2019) a conventional (non nano-doped) CFRP laminate was protected by combining ECF (expanded copper foil) with CNT non-woven mats.

[0006] US2017/291386 discloses a structural component, in particular for an aircraft, spacecraft or rocket, with a ply of fiber reinforced polymer; a first carbon nanotube mat; and a metallic layer. The carbon nanotube mat and the metallic layer are arranged on the ply of fiber reinforced polymer to form a hybrid lightning strike protection layer. The non-woven carbon nanotube mats can be manufactured e. g. by way of a gas-phase catalytic reaction creating a dense cloud of very long carbon nanotubes. These can be collected, for example spun around a drum, to create a non-woven mat. Such non-woven carbon nanotube mats are manufactured e.g. by Tortechn Nano-Fibers Ltd., Israel or Nanocomp Technologies Inc., USA.

[0007] US2016/0031569 discloses a lightning protection layer with a first stratum and a second stratum. The second stratum is coupled to the first stratum along a connecting surface. The first stratum has a metal foil and the second stratum has carbon allotropes.

[0008] Reference 5 (Logakis et al) investigated the influence of multi-wall carbon nanotubes (MWNTs) on the lightning strike performance of carbon fibre. A high temperature aerospace grade epoxy resin was modified with MWNTs. Panels of carbon fibre/epoxy, carbon fibre/epoxy with a protective copper mesh layer, carbon fibre with MWNT modified epoxy, and carbon fibre with copper protection and MWNT modified epoxy were produced.

SUMMARY OF THE INVENTION

[0009] A first aspect of the invention provides a laminate structure comprising: a fibre laminate impregnated with a laminate matrix material; and a veil of carbon nanotubes impregnated with a veil matrix material; wherein the laminate matrix material and the veil matrix material are doped with carbon particles.

[0010] Optionally the veil of carbon nanotubes is not bonded to a metallic lightning strike protection layer.

[0011] Optionally the laminate structure does not comprise a metallic lightning strike protection layer.

[0012] Optionally the veil of carbon nanotubes is bonded to the fibre laminate.

[0013] Optionally the veil of carbon nanotubes is bonded to the fibre laminate by a co-cured joint.

[0014] Optionally the veil of carbon nanotubes is embedded within the fibre laminate. The veil of carbon nanotubes may be embedded within an outer composite ply of the fibre laminate, or embedded between composite plies of the fibre laminate.

[0015] The veil of carbon nanotubes may be embedded under a surface layer of matrix material, wherein the surface layer of matrix material is doped with the carbon particles.

[0016] Optionally the veil of carbon nanotubes is bonded to the fibre laminate by the veil matrix material and/or by a bonding layer which is doped with carbon particles.

[0017] Optionally a concentration of the carbon particles decreases away from the veil in a thickness direction of the fibre laminate.

[0018] Optionally the laminate matrix material is doped with carbon particles at a lower average concentration than the veil matrix material which impregnates the veil of carbon nanotubes.

[0019] Optionally the fibre laminate comprises an outer composite ply which is bonded to the veil of carbon nanotubes and doped with carbon particles.

[0020] Optionally the outer composite ply is doped with carbon particles at a first average concentration; and the veil matrix material is doped with carbon particles at a second average concentration which is different to the first concentration.

[0021] Optionally the fibre laminate comprises a first sub-stack of composite plies which is bonded to the veil of carbon nanotubes; and a second sub-stack of composite plies; wherein the laminate matrix material which impregnates the second sub-stack of composite plies is not doped with carbon particles, or is doped with carbon particles at a lower average concentration than the laminate matrix material which impregnates the first sub-stack of composite plies. In both of these cases, the concentration of the carbon particles decreases away from the veil in a thickness direction of the fibre laminate, and the laminate matrix material which impregnates the second sub-stack is doped with carbon particles at a lower average concentration than the veil matrix material which impregnates the first sub-stack of composite plies (and optionally with zero concentration).

[0022] Optionally the first sub-stack of composite plies is co-cured to the second sub-stack of composite plies.

[0023] Optionally the first sub-stack of composite plies has a smaller thickness than the second sub-stack of composite plies.

[0024] Optionally the first sub-stack of composite plies has a smaller number of composite plies than the second sub-stack of composite plies.

[0025] Optionally the laminate structure has an external surface and an internal surface; and the veil of carbon nanotubes is closer to the external surface than the internal surface.

[0026] Optionally the carbon particles comprise graphene particles and/or carbon nanotubes.

[0027] Optionally the veil of carbon nanotubes comprises a non-woven network of carbon nanotubes.

[0028] Optionally the fibre laminate is a carbon fibre laminate.

[0029] A further aspect of the invention provides an aircraft comprising a laminate structure according to the first aspect.

[0030] Optionally the aircraft comprises a first laminate structure according to the first aspect positioned in a first zone of the aircraft; and a second laminate structure positioned according to the first aspect positioned in a second zone of the aircraft; wherein the laminate matrix material of the first laminate structure is doped with carbon particles at a higher average concentration than the laminate matrix material of the second laminate structure.

[0031] Optionally the first laminate structure is impregnated by the doped laminate matrix material through a full thickness of the fibre laminate.

[0032] A further aspect of the invention provides a method of manufacturing a laminate structure, the method comprising: providing a fibre laminate impregnated with a laminate matrix material; and providing a veil of carbon nanotubes impregnated with a veil matrix material, wherein the laminate matrix material and the veil matrix material are doped with carbon particles, the method further comprising: co-curing the laminate matrix material and the veil matrix material to bond the veil of carbon nanotubes to the fibre laminate.

[0033] Optionally the fibre laminate is provided by laying up a stack of prepreg plies, each prepreg ply comprising one or more fibre layers pre-impregnated with the laminate matrix material.

[0034] Optionally the veil of carbon nanotubes is laid up as a dry veil with the stack of prepreg plies, and the veil matrix material impregnates the veil of carbon nanotubes by flowing into the dry veil from the stack of prepreg plies.

[0035] Optionally the veil of carbon nanotubes is laid up with the stack of prepreg plies as a prepreg veil pre-impregnated with the veil matrix material.

[0036] Optionally the veil matrix material is not doped with the carbon particles when the prepreg veil is laid up, and the veil matrix material becomes doped by the carbon particles flowing into the prepreg veil from the stack of prepreg plies.

[0037] Optionally the fibre laminate is provided by laying up a first sub-stack of prepreg plies, each prepreg ply of the first sub-stack comprising one or more fibre layers pre-impregnated with laminate matrix material; and laying up a second sub-stack of prepreg plies, each prepreg ply of the second sub-stack comprising one or more fibre layers pre-impregnated with laminate matrix material, wherein the laminate matrix material impregnating the second sub-stack is not doped with carbon particles.

[0038] Optionally the laminate matrix material and the veil matrix material are provided by co-infusing the fibre laminate and the veil of carbon nanotubes.

BRIEF DESCRIPTION OF THE DRAWINGS

[0039] Embodiments of the invention will now be described with reference to the accompanying drawings, in which:

[0040] FIG. 1 shows an aircraft;

[0041] FIG. 2 shows a fully doped wing skin panel in cross-section;

[0042] FIG. 3A shows a partially doped fuselage skin panel in cross-section;

[0043] FIG. 3B shows a fuselage skin panel in cross-section with a varying nanoparticle concentration gradient;

[0044] FIG. 4 shows the dry veil and un-cured prepreg components in cross-section in the first step of a method of manufacturing the panel of FIG. 2 or the panel of FIG. 3A;

[0045] FIG. 5 shows the cured laminate components in cross-section resulting from the prepreg method of FIG. 4, where the veil becomes fully embedded in the structural plies;

[0046] FIG. 6 shows the cured laminate components in cross-section resulting from the prepreg method of FIG. 4, where the veil becomes only partially embedded in the structural plies;

[0047] FIG. 7 shows un-cured prepreg components in cross-section in the first step of another method of manufacturing the panel of FIG. 2 or the panel of FIG. 3A; and

[0048] FIG. 8 shows the cured laminate components in cross-section resulting from the prepreg method of FIG. 7, where the veil becomes co-cured to the fibre laminate but not embedded.

DETAILED DESCRIPTION OF EMBODIMENT(S)

[0049] An aircraft 1 shown in FIG. 1 has various lightning strike zones, defined as zones 1-3 in SAE Aerospace Recommended Practices (ARP) 5414. Some zones are more prone to lightning strike than others. Areas in zone 1 are most prone, areas in zone 3 are least prone. By way of example, the wings, the tips of the horizontal tail plane and the nose are mostly in zone 1, whereas most of the fuselage is in zone 2.

[0050] FIG. 2 is a cross-section view of a laminate structure of the aircraft in zone 1, in this case a panel 10 of the skin of one of the wings.

[0051] The panel 10 has an external surface 11 and an internal surface 12, the external surface 11 being positioned such that it is exposed to lightning strike 16.

[0052] The panel 10 is a laminate structure comprising a fibre laminate 13 and a veil 15 of carbon nanotubes. The fibre laminate 13 is a stack of composite plies, each composite ply in the stack comprising a fibre layer impregnated with a laminate matrix material. Optionally each fibre layer in the stack is a carbon fibre layer, although other fibre materials are possible. Optionally the laminate matrix material comprises epoxy resin, although other matrix materials are possible.

[0053] The laminate matrix material which impregnates the fibre laminate 13 is doped with carbon particles. All of the composite plies are doped, so the laminate matrix material is doped through a full thickness T of the fibre laminate 13.

[0054] The carbon particles are formed from an allotrope of carbon. The particles may be 90 wt. % carbon, at least 92 wt. % carbon, or at least 95 wt. % carbon, as determined by elemental analysis.

[0055] Preferably, the carbon particles are carbon nanoparticles.

[0056] The carbon nanoparticles may have at least one dimension less than 500 nm, or more typically at least one dimension less than 100 nm. Most typically the carbon nanoparticles have at least one dimension between 1 nm and 500 nm, or between 1 nm and 100 nm. The dimensions may be determined by microscopy, for example by scanning electron microscopy.

[0057] For the avoidance of doubt, the skilled reader understands that the carbon particles are present in addition to any carbon fibres of the fibre laminate and in addition to the carbon nanotubes of the carbon nanotube veil.

[0058] The term “doping” as used herein is used to refer to incorporation of the particles into the matrix material, for example through mixing. In instances where the particles are carbon nanoparticles, the doping may be referred to as “nano-doping”.

[0059] The carbon particles may be, for example, graphene particles, carbon nanotubes, or mixtures of these components.

[0060] Suitably, the carbon particles are dispersed relative to one another within the laminate matrix material and/or within the veil matrix material. This should be contrasted with the carbon nanotube veil, in which the carbon nanotubes of the veil are associated/aggregated instead of being dispersed. Preferably, there is no or minimal levels of agglomeration and aggregation of the carbon particles, either with other carbon particles or with other components of the laminate structure. Advantageously, ensuring that the carbon particles are dispersed relative to one another helps to reduce the concentration required to form a conductive network from the carbon particles. Doping the carbon particles into the matrix material can allow a conductive network of particles to be formed in three dimensions, which helps to dissipate lightning strike. In addition, doping carbon particles into the matrix material provides a relatively simple route of manufacture.

[0061] Optionally, the carbon particles may be surface-functionalised carbon particles. For example, the surface-functionalised carbon particles may incorporate functional groups at their surface to aid dispersion in the matrix material. Alternatively, or additionally, the carbon particles may incorporate functional groups which reduce or avoid formation of agglomerates of the carbon particles. For example, the carbon particles may be hydroxy-functionalised, carboxy-functionalised, carbonyl-functionalised, amine-functionalised, amide-functionalised or halogen-functionalised. These types of surface functionalisation of the carbon particles may be achieved, for example, according to the methods taught in WO2010/142953 and WO2012/076853.

[0062] Preferably, the carbon particles are graphene particles. The high electrical conductivity of graphene particles (which is higher than, for example carbon black and graphite) means that when graphene particles are used a relatively low loading of particles can be used to establish a conductive network.

[0063] Suitably, the graphene particles have a high aspect ratio. Advantageously, graphene particles having a high aspect ratio can form conductive paths at relatively low loading levels.

[0064] The graphene particles may take the form of particles of monolayer graphene (i.e. a single layer of carbon) or multilayer graphene (i.e. particles consisting of multiple stacked graphene layers). Multilayer graphene particles may have, for example, an average (mean) of 2 to 100 graphene layers per particle. When the graphene particles have 2 to 5 graphene layers per particle, they can be referred to as “few-layer graphene” particles (FLGs). The number of layers may be determined by scanning electron microscopy.

[0065] The graphene particles may take the form of plates/flakes/sheets/ribbons of multilayer graphene material, referred to herein as “graphene nanoplatelets” (the “nano” prefix indicating thinness, instead of the lateral dimensions).

[0066] The graphene particles may take the form of platelets having a thickness less than 100 nm and a major dimension (length or width) perpendicular to the thickness. The platelet thickness is preferably less than 70 nm, preferably less than 50 nm, preferably less than 30 nm, preferably less than 20 nm, preferably less than 10 nm, preferably less than 5 nm (this is based on >90% of the particles having these properties, measured using light scattering by a Zetasizer Ultra). The major dimension is preferably at least 10 times, more preferably at least 100 times, more preferably at least 1,000 times, more preferably at least 10,000 times the thickness. The length may be at least 1 times, at least 2 times, at least 3 times, at least 5 times or at least 10 times the width.

[0067] The graphene particles are preferably at least 90 wt. % carbon based on the bulk (determined by elemental analysis), more preferably at least 92 wt. % carbon, most preferably at least 95 wt. % carbon.

[0068] In a preferred embodiment, the carbon particles may be GNPs (Graphene nanoplatelets) or FLG (few layered graphene), optionally combined with MWCNTs (Multi walled carbon nanotubes).

[0069] The loading of carbon particles in the laminate structure may be, for example, 0.1 wt. % or more, 0.2 wt. % or more, 0.25 wt. % or more, 0.4 wt. % or more, 0.5 wt. % or more, 1 wt. % or more, 2 wt. % or more, 5 wt. % or more, 10 wt. % or more. The upper limit for the loading of carbon particles in the laminate structure may be, for example 1 wt. %, 2 wt. %, 5 wt. %, 10 wt. %. Preferably, the loading of the carbon particles is in the range of, for example, 0.25 to 10 wt. %, 0.5 to 10 wt. %, or 0.5 to 5 wt. %.

[0070] The loading of carbon particles in the laminate structure may be, for example, 0.1 vol. % or more, 0.2 vol. % or more, 0.25 vol. % or more, 0.4 vol. % or more, 0.5 vol. % or more, 1 vol. % or more, 2 vol. % or more, 5 vol. % or more, 10 vol. % or more. The upper limit for the loading of carbon particles in the laminate structure may be, for example, 1 vol. %, 2 vol. %, 5 vol. %, 10 vol. %. Preferably, the loading of the carbon particles is in the range of, for example, 0.25 to 10 vol. %, 0.5 to 10 vol. %, or 0.5 to 5 vol. %. The volume % can be determined by taking a cross-sectional slice through the laminate structure, and examining by size exclusion microscopy.

[0071] Optionally, there is a gradient of carbon particle loading across the thickness of the laminate structure. Preferably, the gradient decreases from the external surface of the laminate structure to the internal surface of the laminate

structure. For example, at least 50% of the carbon particles may be present in the top 50% of the thickness of the laminate structure, in the top 40% of the thickness of the laminate structure, in the top 30% thickness of the laminate structure, in the top 20% thickness of the laminate structure (the “top” of the structure being the external surface). Optionally, 100% of the carbon particles may be present in the top 50% of the thickness of the laminate structure, in the top 40% of the thickness of the laminate structure, in the top 30% thickness of the laminate structure, or in the top 20% thickness of the laminate structure. The concentration of carbon particles may be determined by examining a cross-sectional slice of the laminate structure under a scanning electron microscope.

[0072] The stack of composite plies comprises an outer ply **14** which, along with the other plies in the fibre laminate **13**, is doped with the carbon particles.

[0073] The veil **15** of carbon nanotubes is bonded to the outer ply **14** of the fibre laminate. The veil **15** is configured to provide lightning strike protection to the panel **10**. The veil **15** may be a non-woven network of intermingled carbon nanotubes with substantially random orientation.

[0074] The carbon nanotubes of the veil **15** may be multi-walled nanotubes (MWNTs), single-walled nanotubes (SWNTs) or a mixture thereof.

[0075] At least some of the carbon nanotubes of the veil **15** may have an aspect ratio greater than 1000:1, greater than 5,000:1, or greater than 10,000:1.

[0076] Typically a thickness of the veil **15** is less than 100 microns (100×10^{-6} m) or less than 50 microns (50×10^{-6} m). Most preferably a thickness of the veil **15** is less than 30 microns (30×10^{-6} m). Alternatively the thickness of the veil **15** may be more than 100 microns (100×10^{-6} m).

[0077] The veil **15** is closer to the external surface **11** than the internal surface **12**. FIG. 2 shows the veil **15** as forming the external surface, but alternatively the veil may be embedded within the outer ply **14** so that the outer ply **14** and the embedded veil **15** together form the external surface **11** of the panel **10**. Note that the outer ply **14** and the embedded veil **15** may be covered with one or more surface layers, such as paint.

[0078] The veil **15** of carbon nanotubes is impregnated with a veil matrix material which is also doped with carbon particles. The carbon particles are as described above.

[0079] Optionally the veil matrix material comprises an epoxy resin, although other resin materials are possible. In this case the veil matrix material is the same type of material (for instance the same type of epoxy resin) as the laminate matrix material impregnating the fibre laminate **13**.

[0080] FIG. 3A is a cross-sectional view of a laminate structure of the aircraft in zone 2, in this case a panel **10a** of the skin on the fuselage.

[0081] Certain elements of the panel **10a** have equivalents in the panel **10**. These elements are given the same reference number, appended by the letter “a”. Where the elements are identical, they will not be described again.

[0082] The panel **10a** is a laminate structure comprising a fibre laminate **13a** and a carbon nanotube veil **15a**. The fibre laminate **13a** comprises a first sub-stack **16** of composite plies and a second sub-stack **17** of composite plies. The first sub-stack **16** is co-cured to the second sub-stack **17** and to the veil **15a** of carbon nanotubes

[0083] The laminate matrix material which impregnates the first sub-stack **16** is doped with carbon particles, whereas

the laminate matrix material which impregnates the second sub-stack **17** is not doped with carbon particles.

[0084] Thus only some of the composite plies of the panel **10a** are doped, so that the fibre laminate **13a** is only doped through a partial thickness **T1**.

[0085] The laminate matrix material of all of the composite plies in the first sub-stack **16** (including the outer ply **14a**) is doped with the carbon particles.

[0086] The laminate matrix material may be doped with graphene particles, with carbon nanotubes, or with a mixture of graphene particles and carbon nanotubes.

[0087] Advantageously, the panel **10a** may be manufactured in prepreg, as described in more detail below with reference to FIGS. 4-8 which will be described later.

[0088] Another panel **10b** which may be located in zone 2 of the aircraft is shown in FIG. 3B. Certain elements of the panel **10b** have equivalents in the panel **10a**. These elements are given the same reference number, appended by the letter “b”. Where the elements are identical, they will not be described again.

[0089] The only difference between the panel **10a** and the panel **10b** is that the laminate matrix material which impregnates the second sub-stack **18** in the panel **10b** is doped with the same carbon particles as the first sub-stack **16b**, but at a lower average concentration than the laminate matrix material which impregnates the first sub-stack **16b**.

[0090] In one example the second sub-stack **18** may have a relatively low and uniform concentration of carbon particles.

[0091] In another example, a concentration of the carbon particles may decrease continuously in the second sub-stack **18** away from the veil **15b** in a thickness direction of the fibre laminate. Thus the carbon particle concentration is relatively high in the veil **15b** and in the first sub-stack **16b**, but decreases continuously through the second sub-stack **18**—potentially to zero concentration at the bottom of the second sub-stack **18**. This concentration gradient may be achieved by manufacturing the panel **10b** by resin co-infusion, as described in more detail below.

[0092] The panels **10a**, **10b** can be manufactured more cheaply than the highly doped panel **10**, because fewer carbon particles are required (note that carbon particles such as graphene can be expensive).

[0093] The first sub-stack **16**, **16b** is the outer part of the stack, positioned between the veil **15a**, **15b** and the second sub-stack **17**, **18**.

[0094] The first sub-stack **16**, **16b** may have a smaller stack thickness **T1** than the stack thickness **T2** of the second sub-stack **17**, **18**.

[0095] The first sub-stack **16**, **16b** may have a smaller number of composite plies than the second sub-stack **17**, **18**.

[0096] By way of non-limiting example, the thickness **T1** may be of the order of 2 mm (about 10 to 20 plies) and the thickness **T2** may be of the order of 20 mm (about 100 to 200 plies). Alternatively the thickness **T1** may be much lower—potentially as little as a single ply.

[0097] The fibre laminate **13** of the panel **10** may be impregnated by the doped laminate matrix material through a thickness **T** which is greater than the thickness **T1** of the first sub-stack **16**, **16b**. This gives the panel **10** enhanced lightning strike protection, compared with the panels **10a**, **10b**.

[0098] The panel **10** may be positioned in zone 1 of the aircraft (as defined in in SAE Aerospace Recommended

Practices (ARP) 5414) and the panels **10a**, **10b** may be positioned in zone 2 (as defined in SAE Aerospace Recommended Practices (ARP) 5414). The fibre laminate of the panel **10** is impregnated by the doped laminate matrix material through its full thickness **T**, whereas the fibre laminate of the panel **10a**, **10b** may be impregnated by the doped laminate matrix material through only part of its thickness.

[0099] In both FIG. **3A** and FIG. **3B**, the concentration of the carbon particles decreases away from the veil in a thickness direction of the fibre laminate. In the case of FIG. **3A** the concentration decreases in a step down to zero where the first sub-stack **16** meets the second sub-stack **17**. In the case of FIG. **3B** the concentration decreases continuously through the thickness of the second sub-stack **17**.

[0100] In both FIG. **3A** and FIG. **3B**, the laminate matrix material which impregnates the second sub-stack **17**, **18** is doped with carbon particles at a lower average concentration than the veil matrix material which impregnates the first sub-stack **16**, **16b**. In the case of FIG. **3A**, the second sub-stack **17** has a concentration of zero.

[0101] The laminate matrix material of the first laminate structure (panel **10**) of FIG. **2** is doped with carbon particles at a higher average concentration than the laminate matrix material of the second laminate structure (panel **10a** or **10b**) of FIG. **3A** or **3B**.

[0102] Various prepreg methods of manufacturing the panels **10**, **10a** are shown in FIGS. **4-8**.

[0103] Referring first to FIG. **4**, a dry veil **15'** of carbon nanotubes is placed on a mould tool surface **18** of a mould tool. The dry veil **15'** may be obtained by various fabrication methods. One method involves injecting a precursor, followed by nucleation of the CNTs in a reactor, at very high temperature. A “sock” of uniform diameter (0.5-1 metre) emerges and is wound on a drum. The “sock” walls are made from long intermingled CNTs, with random orientation, but biased towards the extraction direction.

[0104] The CNTs, originating in the reactor, are streamed in a turbulent flow. Turbulent flow is random in nature, and when the CNTs are streamed in such flow they become intermingled, similar to vermicelli or boiled spaghetti.

[0105] Reference **6** (Wang et al) outlines a variation of this manufacturing process.

[0106] Another method of manufacturing the dry veil **15'** is to grow a “forest” of CNTs on a substrate, then treat the “forest” so the CNTs tilt in random directions to form a flattened layer. By way of example, the CNTs may be flattened by a calendaring process that randomly flattens the CNT “forest” on a 2D substrate. The CNTs are not perfectly vertical and parallel to with each other, and they “fall” in the direction they are leaning.

[0107] The fibre laminate **13**, **13a** is then laid up on top of the dry veil **15'** as a stack of prepreg plies, each prepreg ply comprising one or more fibre layers pre-impregnated with either doped laminate matrix material or un-doped laminate matrix material (i.e., matrix material which is not doped with carbon particles). In the case of panel **10**, all of the prepreg plies are doped; in the case of the panel **10a** only the lower prepreg plies (i.e. the plies of the first sub-stack **16**) are doped and the others are un-doped.

[0108] FIG. **4** shows an outer prepreg ply **14'**, and the next prepreg ply **27'** in the stack. Each prepreg ply comprises one or more layers of unidirectional carbon fibre pre-impregnated with laminate matrix material. For example the outer

prepreg ply **14'** comprises a layer of unidirectional carbon fibre **20** pre-impregnated with doped laminate matrix material **21**; and the next prepreg ply **27'** comprises a layer of unidirectional carbon fibre **22** pre-impregnated with doped laminate matrix material **23**. The prepreg plies **14'**, **27'** are laid up in contact with each other as shown. The outer prepreg ply **14'** is in contact with the dry veil **15'**.

[0109] The directions of the unidirectional carbon fibres may vary from ply to ply in the stack of prepreg plies, and each ply may also have more than one orientation.

[0110] The stack of prepreg plies is then compressed/consolidated by a vacuum bag and then cured in an autoclave at a pressure of several bars. The prepreg plies are heat cured in contact with the dry veil **15'**, so that the dry veil **15'** becomes infused and bonded to the stack of composite plies, to form the cured and impregnated veil **15** or **15a**. More specifically, the thermosetting doped laminate matrix material is heated, softens, melts and partially flows into the dry veil **15'** of carbon nanotubes from the stack of prepreg plies **14'**, **27'**, coalesces at the interfaces between the prepreg plies, and then co-cures to bond the prepreg plies together and to bond the impregnated veil **15** to the outer ply **14** of the stack as shown in FIG. **5**.

[0111] FIG. **5** shows the parts in their impregnated and cured state corresponding with FIGS. **2** and **3A**: namely the veil **15**, **15a** the outer composite ply **14**, **14a** and the next composite ply **27** in the stack. FIGS. **4** shows the parts in their dry or uncured state—namely the dry veil **15'**, the uncured outer prepreg ply **14'** and the uncured prepreg ply **27'**.

[0112] In the cured structure of FIG. **5**, the carbon fibre layers **20**, **22** are bonded together by a co-cured joint comprising a cured layer **24** of doped laminate matrix material. During the curing process, the dry fibre veil **15'** may become fully embedded in the outer ply **14**. In this case, the veil **15**, **15a** in the cured structure of FIG. **5** is bonded to the fibre laminate **13**, **13a** by the cured veil matrix material which impregnates the veil **15**, **15a** and the cured laminate matrix material which impregnates the carbon fibre layer **20**.

[0113] The veil **15**, **15a** is also embedded in the fibre laminate under a surface layer **25** of cured doped matrix material between the veil **15**, **15a** and the surface **18** of the mould tool.

[0114] Thus the veil **15**, **15a** is bonded to the outer ply **14** of the fibre laminate by a co-cured joint between the veil **15**, **15a** and the carbon fibre layer **20**, and a co-cured joint between the veil and the surface layer **25**.

[0115] In the fully embedded case of FIG. **5**, some carbon nanotubes of the veil **15**, **15a**, in the cured structure are in contact with the layer of unidirectional carbon fibre **20** and some carbon nanotubes of the veil **15**, **15a** are in contact with the carbon particles which are mixed within the doped veil matrix material.

[0116] The veil **15**, **15a** of carbon nanotubes is embedded under a surface layer **25** of matrix material, and the surface layer **25** of matrix material is doped with carbon particles. Thus some carbon nanotubes of the veil **15** are in contact with the carbon particles which are mixed within the surface layer **25**.

[0117] Note that the layers in FIGS. **4** and **5** are illustrated schematically, and not to scale. The veil **15**, **15a** is typically much thinner than each prepreg ply **14'**, **27'**. By way of example, each prepreg ply **14'**, **27'** may have a thickness of

the order of 0.1-0.5 mm (100-500 micron) after it has cured, and the veil 15, 15a may have a thickness less than 30 micron after it has cured.

[0118] In an alternative shown in FIG. 6, during the curing process the dry veil 15' becomes only partially embedded in the outer ply 14, so that the veil 15, 15a in the cured structure is not in contact with the layer 20 of unidirectional carbon fibre. The veil 15, 15a in the case of FIG. 6 is bonded to the fibre laminate by a co-cured joint comprising a cured bonding layer 26 of doped laminate matrix material.

[0119] In a further alternative (not shown) the partially embedded dry veil 15' of FIG. 6 may be embedded under a surface layer of doped matrix material like the surface layer 25 of FIG. 5, whilst remaining separated from the layer 20 by the cured bonding layer 26.

[0120] The veil matrix material which impregnates the veil 15, 15a in the cured structure of FIG. 5 or FIG. 6 flows into the dry veil 15' from the stack of prepreg plies 14', 27'. Thus the veil matrix material is doped with carbon particles at a similar concentration to the laminate matrix material which impregnates the fibre laminate 13, 13a.

[0121] In an alternative prepreg manufacturing method shown in FIG. 7, the veil is laid up on the tool 18 as a prepreg veil 15" which is pre-impregnated with the veil matrix material. The veil matrix material in the prepreg veil 15" may be doped with the same carbon particles as the prepreps of the fibre laminate 13, 13a, or it may be un-doped—i.e. not doped with carbon particles.

[0122] The use of a prepreg veil 15" may be preferred, because it is easier to handle than a dry veil 15'.

[0123] During the co-curing process, the prepreg veil 15" may become fully embedded in the outer ply 14 (so the veil 15, 15a in the cured structure contacts the layer of unidirectional carbon fibre 20 as in FIG. 5); it may become partially embedded in the outer ply 14 (so the veil 15, 15a in the cured structure does not contact the layer 20 of unidirectional carbon fibre but is embedded under a surface layer of matrix material); or it may not become embedded at all (as shown in FIG. 8).

[0124] If the veil matrix material in the prepreg veil 15" is un-doped, then the cured veil matrix material which impregnates the veil 15, 15a in the cured structure will contain some carbon particles which originated in the doped matrix material 21 of the outer prepreg ply 14' and flowed or diffused into the veil 15, 15a.

[0125] If the veil matrix material in the prepreg veil 15" is un-doped, and the veil becomes fully embedded as in FIG. 5, or partially embedded, then the matrix material of the surface layer 25 may be un-doped, or it may contain carbon particles which originated in the doped matrix material 21 of the outer prepreg ply 14a and flowed or diffused through the prepreg veil 15" and into the surface layer 25.

[0126] In the cured structure of FIG. 8, during the co-curing process the prepreg veil 15" does not become embedded in the outer ply 14, so the veil 15, 15a in the cured structure is not in contact with the layer of unidirectional carbon fibre 20 and is not embedded under a surface layer. The veil 15 in this case is bonded to the outer ply 14 of the fibre laminate by a co-cured joint comprising a cured bonding layer 28 of doped laminate matrix material.

[0127] If the veil matrix material in the prepreg veil 15" is un-doped, then the matrix material of the cured bonding layer 28 will contain carbon particles which originated in the doped matrix material 21 of the outer prepreg ply 14'.

[0128] The cured veil matrix material which impregnates the veil in FIG. 8 will also contain some carbon particles which flowed or diffused into the veil from the doped matrix material 21 of the outer prepreg ply 14'.

[0129] The prepreg methods of FIGS. 4-8 are well suited to manufacturing the panel 10a of FIG. 3A. In this case the fibre laminate 13a is provided by laying up a first sub-stack of prepreg plies, each prepreg ply of the first sub-stack comprising one or more fibre layers pre-impregnated with doped laminate matrix material; and laying up a second sub-stack of prepreg plies, each prepreg ply of the second sub-stack comprising one or more fibre layers pre-impregnated with un-doped laminate matrix material. The un-doped laminate matrix material which impregnates the prepreg plies of the second sub-stack is not doped with carbon particles.

[0130] In some of the prepreg methods described above, the veil matrix material is un-doped when the prepreg veil 15" is laid up, and the veil matrix material becomes doped by carbon particles flowing into the prepreg veil 15" from the stack of prepreg plies. In this case, a concentration of the carbon particles may be lower, on average, in the cured veil matrix material than in the cured laminate matrix material. Surprisingly, despite this lower average concentration, it has been found that starting from a prepreg veil 15" with an un-doped veil matrix material results in a better lightning strike performance compared with starting from a dry veil 15'. Without being bound by theory, it is speculated that this improved performance may be due to carbon particles diffusing to the outer surface of the veil 15, 15a, optionally into a surface layer such as the surface layer 25. The doped laminate matrix material will have a slightly higher density than the un-doped veil matrix material in the prepreg veil 15". This enables an easy migration of the carbon particles from the outer prepreg ply 14' to the outer surface of the prepreg veil 15". This may result in a surface layer in the cured laminate structure with a higher concentration of carbon particles than within the body of the veil 15, 15a. This surface layer may provide an improved "Faraday cage", resulting in the observed better lightning strike performance. For instance, in the case of FIG. 5 the laminate structure may comprise a surface layer 25 of matrix material with a higher concentration of carbon particles than the veil matrix material within the veil 15, 15a.

[0131] A preferred method of manufacturing the panel 10b of FIG. 3B is co-infusion. In the co-infusion method, the fibre laminate 13b is laid up as a stack of porous dry fibre preforms, along with a dry veil of carbon nanotubes, similar to the dry veil 15'. The dry fibre preforms and the dry veil are then co-infused with liquid doped matrix material, which is then cured to co-cure the various parts together.

[0132] The doped matrix material flows into the first sub-stack 16b through the dry veil, then flows into the second sub-stack 18 from the first sub-stack. The veil provides a filtering effect, which causes the carbon particles to accumulate inside the veil and in the first sub-stack 16b, with relatively few carbon particles reaching the second sub-stack 18. This creates a concentration gradient in the cured structure, the concentration of carbon particles decreasing away from the veil 15b in the thickness direction of the laminate structure.

[0133] In all of the methods described above, the fibre laminate comprises an outer composite ply 14, 14a, 14b which is bonded to the veil 15, 15a, 15b of carbon nanotubes

and doped with carbon particles. The outer composite ply **14**, **14a**, **14b** is doped with carbon particles at a first average concentration; and the veil matrix material is doped with carbon particles at a second average concentration. In some cases, the first average concentration and the second average concentration may be the same—for instance in the prepreg processes which start with a dry veil **15'** or a doped prepreg veil **15''**. In other cases, the first average concentration and the second average concentration may be different to each other. For instance starting from of an un-doped prepreg veil **15'** may result in a lower second average concentration in the veil, and the co-infusion method may result in a higher second average concentration in the veil.

[0134] The mixing of the different carbon particles into the matrix material may follow well known processes involving either two or three roll milling and/or insonification using a sonotrode to convey ultra-sonic energy into an epoxy resin masterbatch. This doped masterbatch is then thoroughly diluted with the main resin, either in a pre-preg line (to produce the prepregs **14'**, **27'**, **15''**) or in an infusion mixing-dosing apparatus (in the case of the co-infusion process described above).

[0135] There is a good correlation between effective lightning strike protection and the measured, in plane, electrical conductivity of a carbon-fibre reinforced polymer (CFRP) laminate. Up until recently, these measurements were done using contact probes that required careful coupon preparation (silver/gold coating the probe contact areas). This was an unreliable method for CFRP and thus a contactless, more accurate method (the “Gobin” method) was developed and is now used. The Gobin method relies on electromagnetic field attenuation, measured when a CFRP panel is placed between two probes that is then correlated to the electrical conductivity of a known value from a reference coupon.

[0136] Another textbook attempt to determine protection effectiveness of CFRP structures by predicting its electrical conductivity, is by calculating its dielectric relaxation time; it is related to the electrical conductivity and in essence it measures the time it takes a charged system to return to equilibrium; the issue is that the mathematical model is only accurate for semi-conductors, not metals.

[0137] From the earlier contact based electrical conductivity measurements it was established that medium weight expanded copper foil (ECF) has a value of 4×10^7 S/m; CFRP along the fibre, 1×10^4 S/m; CNT & graphene estimated at $< 1 \times 10^8$ S/m.

[0138] Theoretical calculation applying the rule of mixtures on the volume fraction content of a CFRP laminate with 60% of carbon fibres and 1% of nano-fillers+CNT veil: $0.6(10^4/0.6) + 0.4(10^8/0.01) \sim 4 \times 10^9$ S/m

[0139] This value falls short of the expected conductivity values as experimentally measured by contact methods but is in line with contactless measurements recently obtained.

[0140] The lightning strike phenomenon is yet to be fully understood due to its transient nature, where pressure and heat occur in fractions of seconds, and thus offers significant challenges for an accurate mathematical model.

[0141] It has been established that there are two main lightning strike damage effects: thermal effects and mechanical force effects. The latter are transient by nature, while the former are of a relatively long duration.

[0142] Thermal effects involve not only conductive heat from the arc plasma channel, but also Joule heating (current flow through the conductive materials) and plasma channel

heat radiation. This results in temperature-induced material degradation and mechanical strains due to expansion/contraction.

[0143] The mechanical force effects include magnetic field pressure (current flow through the conductive materials), shock waves due to supersonic expansion of the plasma channel and also from chemical sublimation.

[0144] Surprisingly, it has been established by test that most of the damage to CFRP structures appears to result from the mechanical force effects, not thermal effects.

[0145] Where expanded copper foil (ECF) is used, as in Reference 4, transient explosive forces develop severe impact loads by the vaporized particles of copper protection foil, resin and carbon fibre. The highly dense copper particles are believed to be responsible for the bulk of the damage.

[0146] The laminate structures **10**, **10a**, **10b** described above have no metallic lightning strike protection layer, such as an ECF layer. It is believed that the removal of the high density (~ 9) ECF layer, substituted by a lower density, highly conductive veil **15**, **15a**, **15b** of carbon nanotubes (with a density of 1.4) will significantly reduce the mechanical force damage.

[0147] Further, it is believed that the randomly oriented intermingled carbon nanotubes in the veil may be more efficient at absorbing energy than an ECF lattice-like layer.

[0148] Further, it is believed that there may be a synergistic effect in combining a doped fibre laminate with a doped carbon nanotube veil. The carbon nanotube veil provides the advantages mentioned above: it reduces mechanical force effects due to its low density and intermingled structure. Impregnating the veil with a veil matrix material which is doped with carbon particles may further improve the lightning strike performance, because the carbon nanotubes of the veil interact with the carbon particles in the veil matrix material in order to improve the conductive network (increase the amount of conductive paths) available to dissipate electrical energy.

[0149] In the examples above, the veil **15**, **15a**, **15b** of carbon nanotubes is bonded to the fibre laminate **13**, **13a**, **13b** by the veil matrix material and/or by a bonding layer **26**, **28** which is doped with carbon particles. This is preferred, although in an alternative embodiment the veil **15**, **15a**, **15b** of carbon nanotubes may be bonded to the fibre laminate **13**, **13a**, **13b** by an un-doped bonding layer.

[0150] In the examples above, the veil **15**, **15a**, **15b** of carbon nanotubes is bonded to the surface layer **14**, **14a**, **14b** of the fibre laminate, and optionally also embedded within the surface layer **14**, **14a**, **14b** of the fibre laminate. In other embodiments, the veil **15**, **15a**, **15b** of carbon nanotubes may be embedded in the fibre laminate between the surface layer **14**, **14a**, **14b** and the next composite ply **27**. In all of these cases, the veil **15** of carbon nanotubes is bonded to the fibre laminate **13**, **13a**, **13b** by a co-cured joint. A co-cured joint typically has substantially no interface in the cured structure.

[0151] In other embodiments the veil **15**, **15a**, **15b** of carbon nanotubes may be bonded to the fibre laminate **13**, **13a**, **13b** by some other bonding process, such as co-bonding or secondary bonding. In this case, the veil **15**, **15a**, **15b** of carbon nanotubes in the cured structure will be bonded to the fibre laminate **13**, **13a**, **13b** by another type of adhesive joint, such as a co-bonded joint or a secondary-bonded joint.

[0152] In the examples above the wing skin panel **10** is highly doped through its full thickness, whereas the fuselage

panels 10a, 10b are not. Other variations are possible. For instance, some parts of the aircraft (for instance the stringers which run along the span of each wing on the inside of the wing skin) are more prone to edge glow than others. Thus the stringers may be doped through their full thickness with carbon particles (like the panel 10) whereas other parts less prone to edge glow (for instance the wing skin) may only be highly doped through part of their thickness (like the panel 10a or the panel 10b).

[0153] Where the word ‘or’ appears this is to be construed to mean ‘and/or’ such that items referred to are not necessarily mutually exclusive and may be used in any appropriate combination.

[0154] Although the invention has been described above with reference to one or more preferred embodiments, it will be appreciated that various changes or modifications may be made without departing from the scope of the invention as defined in the appended claims.

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1. A laminate structure comprising:
a fibre laminate impregnated with a laminate matrix material; and
a veil of carbon nanotubes impregnated with a veil matrix material;
wherein the laminate matrix material and the veil matrix material are doped with carbon particles.

2. A laminate structure according to claim 1 wherein the veil of carbon nanotubes is not bonded to a metallic lightning strike protection layer or the laminate structure does not comprise a metallic lightning strike protection layer.

3. A laminate structure according to claim 1, wherein the veil of carbon nanotubes is bonded to the fibre laminate.

4. (canceled)

5. A laminate structure according to claim 1, wherein the veil of carbon nanotubes is embedded within the fibre laminate.

6. A laminate structure according to claim 5 wherein the veil of carbon nanotubes is embedded within an outer composite ply of the fibre laminate.

7. (canceled)

8. A laminate structure according to claim 1, wherein the veil of carbon nanotubes is bonded to the fibre laminate by the veil matrix material and/or by a bonding layer which is doped with carbon particles.

9. A laminate structure according to claim 1, wherein a concentration of the carbon particles decreases away from the veil in a thickness direction of the fibre laminate.

10. A laminate structure according to claim 1, wherein the laminate matrix material is doped with carbon particles at a lower average concentration than the veil matrix material which impregnates the veil of carbon nanotubes.

11. A laminate structure according to claim 1, wherein the fibre laminate comprises an outer composite ply which is bonded to the veil of carbon nanotubes and doped with carbon particles.

12. A laminate structure according to claim 11, wherein the outer composite ply is doped with carbon particles at a first average concentration; and the veil matrix material is doped with carbon particles at a second average concentration which is different to the first concentration.

13. A laminate structure according to claim 1, wherein the fibre laminate comprises a first sub-stack of composite plies which is bonded to the veil of carbon nanotubes; and a second sub-stack of composite plies; wherein the laminate matrix material which impregnates the second sub-stack of composite plies is not doped with carbon particles, or the second sub-stack of composite plies is doped with carbon particles at a lower average concentration than the laminate matrix material which impregnates the first sub-stack of composite plies.

14. A laminate structure according to claim 1, wherein the laminate structure has an external surface and an internal surface; and the veil of carbon nanotubes is closer to the external surface than the internal surface.

15. A laminate structure according to claim 1, wherein the carbon particles comprise or consist of graphene particles and/or carbon nanotubes.

16. A laminate structure according to claim 1, wherein the carbon particles are carbon nanoparticles.

17. An aircraft comprising a laminate structure according to claim 1.

18. An aircraft according to claim 17, comprising a first laminate structure including a fibre laminate impregnated with a laminate matrix material, a veil of carbon nanotubes impregnated with a veil of matrix material, wherein the laminate matrix material and the veil matrix material are doped with carbon particles, wherein the first laminate structure is positioned in a first zone of the aircraft; and a second laminate structure including a fibre laminate impregnated with a laminate matrix material, a veil of carbon nanotubes impregnated with a veil of matrix material, wherein the laminate matrix material and the veil matrix material are doped with carbon particles, wherein the second laminate structure is positioned in a second zone of the aircraft; wherein the laminate matrix material of the first laminate structure is doped with carbon particles at a higher

average concentration than the laminate matrix material of the second laminate structure.

19. (canceled)

20. A method of manufacturing a laminate structure, the method comprising;

providing a fibre laminate impregnated with a laminate matrix material; and

providing a veil of carbon nanotubes impregnated with a veil matrix material,

wherein the laminate matrix material and the veil matrix material are doped with carbon particles, the method further comprising:

co-curing the laminate matrix material and the veil matrix material to bond the veil of carbon nanotubes to the fibre laminate.

21. A method according to claim 20 wherein the fibre laminate is provided by laying up a stack of prepreg plies, each prepreg ply comprising one or more fibre layers pre-impregnated with the laminate matrix material.

22. (canceled)

23. (canceled)

24. (canceled)

25. A method according to claim 20, wherein the fibre laminate is provided by laying up a first sub-stack of prepreg plies, each prepreg ply of the first sub-stack comprising one or more fibre layers pre-impregnated with the laminate matrix material; and laying up a second sub-stack of prepreg plies, each prepreg ply of the second sub-stack comprising one or more fibre layers pre-impregnated with laminate matrix material, wherein the laminate matrix material impregnating the second sub-stack is not doped with carbon particles.

26. A method according to claim 20 wherein the laminate matrix material and the veil matrix material are provided by co-infusing the fibre laminate and the veil of carbon nanotubes.

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