Abstract: A composite shielding material in the form of syntactic foam where the spherical or spherical-like articles are encompassed by an organic or inorganic matrix material, and coated with a layer of nanostructures such as carbon nanotubes, graphene, graphene flakes. Such articles may be alternatively or additionally be covered with nano-sized metal particles and the mould is filled with organic or inorganic matrix, and micro and/or nano-sized reinforcement elements. Such material possesses both reflective and absorptive properties to improve shielding effectiveness. Also process for making the same is disclosed. The composite material can be used as an electromagnetic, thermal or acoustic shield.
A COMPOSITE SHIELDING MATERIAL AND A PROCESS OF MAKING THE SAME

FIELD OF INVENTION

This invention relates generally to thermal, electromagnetic and acoustic composite shielding materials and, more particularly, to a composite shielding material in the form of syntactic foam comprising of spherical or spherical-like articles coated with a layer of nanostructures such as carbon nanotubes, graphene, graphene flakes, metals and/or alloys. Such articles may be additionally covered with nano-sized metal particles. The spherical or spherical-like articles are encompassed by an organic or inorganic matrix material, and preferably with micro and/or nano-sized reinforcement elements. Such material possesses both reflective and absorptive properties to improve shielding effectiveness. Also process for making the same is disclosed. The composite material can be used as a thermal, electromagnetic or acoustic screen and/or absorber.

BACKGROUND ART

Electromagnetic radiation from high intensity sources can have adverse effects on human health. Likewise, noise and vibration can not only impair health but also have a negative effect on the productivity. The new material would offer a superior alternative for example in shielding rooms in public areas for electromagnetic fields' risk groups (maternity hospitals, hospitals, kindergartens, schools, etc.). In long-term perspective, the implementation of such shields would improve environmental health conditions and result in a positive effect on population's health.

In the automotive industry, the use of the new material as a shock absorbent may save lives and allow reduction of injuries from traffic collisions. Lightweight material would open new avenues for the aerospace industry. Civil construction domain would gain a new construction material, which would allow shielding houses or rooms from high level electromagnetic fields, infrared radiation, and mechanical, including acoustic vibration. Due to the electromagnetic (EM) shielding properties of the material, it could also be used to reduce the risk of industrial espionage from electronic eavesdropping.

There is already known shielding fabric Aaronia-Shield® EMC and RFI. Fabric is made of silver as screening material, and polyamide as carrier material. The transparent, washable, antiseptic RF shielding is optimal for usage as RF window protection, fly screens,
curtains [1]. But this material has very high cost and is not high heat resistant. Also, due to material structure fabric is not well fit to heavy-industry or armour components protection.

Known is [2] a lightweight microcellular polyetherimide (PEI)/graphene nanocomposite foams with a density of about 0.3 g/cm³ by a phase separation process. It was observed that the strong extensional flow generated during cell growth induced the enrichment and orientation of graphene on cell walls. The foaming process significantly increased the specific EM shielding effectiveness from 17 to 44 dB/(g/cm³). However, the general properties of these polymers, such as low heat-resistance, poor flame retardancy, and smoke generation, restrict their use as EM shielding material with satisfactory shielding effectiveness (SE) materials in aerospace and other special fields. As well necessary to admit complex multi-stage preparation process of this material such as: long-time and multi stage mixing and vigorous stirring. The drawback of this process is a difficulty of uniform distribution of NS in matrix volume, lack of 100% covering of NS through the material cross-section.

Known are [3] syntactic foams, which can be synthesized by mechanical mixing of hollow microspheres with a matrix material. In this work, a surface modification method employing polydopamine as a surface treatment agent for hollow carbon microspheres (HCM) was used. The silver coated HCM (Ag-PDA-HCMs) impacted the complex permittivity of the syntactic foams leading to high EM shielding effectiveness. The specific EM shielding effect reached up to 46.3 dB·cm³/g, demonstrated the Ag-PDA-HCMs/epoxy syntactic foam as a promising candidate for lightweight high-performance EM shielding material. The drawback is complicated multi-stage preparation process as well as of HCM, as (Ag-PDA-HCMs) including such process as freeze-drying and other; used carbon HS, which is oxidising and combustible (by O₂ at high temp) material comparing to ceramic hollow spheres, used in the claimed patent.

Known is [4] spherical core (polystyrene, PS)/shell (polypyrrole, PPy) synthesized via in situ chemical oxidative copolymerization of pyrrole (Py) on the surface of sulfonated PS microsphere followed by the formation of hollow polypyrrole (HPPy) shell by dissolving PS inner core in THF. Thereafter, it has been found that such fabricated novel art of morphology acts as a conducting trap in absorbing electromagnetic (EM) wave by internal reflection.
Material has EM SE of HPPy (30-35 dB) significantly higher compared to PPy (20-5 dB) in the frequency range of 0.5-8 GHz due to the trapping of EM wave by internal reflection.

Patent [5] discloses an EM shielding material, consisting of one or more electromagnetic wave-shielding layers and one or more surface layers. The shielding layers are comprised of a thermoplastic resin, an aluminium or aluminium alloy and electrically conductive carbon black. However, it is very difficult to provide flame resistance to compositions containing large amounts of carbon black.

Patent [6] discloses electrically conductive materials that can be used to shield EM radiation, whereas energy-absorptive materials can be used to suppress EM radiation. Disclosed are systems and processes for combining electrically conductive and absorptive materials to improve EM shielding effectiveness. In one embodiment, an absorptive material is combined with the conducting material forming a composite. In another embodiment, absorptive material is combined with electrically conductive material and selectively applied to a substrate, such as a plastic enclosure, to suppress EM radiation incident upon the substrate, thereby reducing the susceptibility of electronics contained within across a broad frequency range.

Since noise problem has become much more complicated and serious and the demands for a better environment and more diversified life styles increase, thin, lightweight and low-cost materials that absorb sound waves in wider frequency regions are strongly desired. Accordingly, researchers have paid much attention to the sound absorbing features of varied granular or particle materials [7-9]. To name a few, metallic hollow spheres were applied as sound absorber for the reduction of noise [8], and ceramic hollow spherical beads were used to prepare acoustic materials [10].

Work [9] describes cement and asphalt concrete specimens with different volume fractions of cenospheres and varying diameter and thickness that were tested to determine their acoustic characteristics over the range of frequencies (0-4000 Hz). Experimental results showed that a 40% volume fraction addition of cenospheres to cement matrix increased the noise reduction coefficient by 100%.

Patent [11] describes similar approach, of involving NS into matrix, where homogeneously mixing 0-20% by weight of carbon nanotubes and 30-90% by weight of resin
matrix under continuous stirring, with the addition of stoichiometric quantity of a hardener in case of epoxy resin, or with the addition of stoichiometric quantity of a catalyst mixture in case of cyanate ester resin; additionally adding 10-60% by weight of glass hollow microspheres HMS to the homogeneous mixture in step (a) to get an uniform dough. With following curing the dough at room temperature for about 24 hours, or at elevated temperatures from 80 to 180°C for about 2-4 hours and subsequent post curing at elevated temperatures from 100 to 350°C for about 2-4 hours depending upon the resin system to form a syntactic foam. The drawbacks of this solution are non-uniform distribution of NS in matrix volume, lack of 100% covering of NS through the material cross-section, used glass HMS, with low (550-650°C) softening temperature. Additionally, cyanate ester resin were used, which is potentially harmful for humans, especially in fire accident when hydrogen cyanide (HCN) evaporates.

Patent [12] describes design and development of carbon nanotubes (CNT) reinforced electrically conducting synthetic foams comprising resin matrix system, carbon nanotubes, hollow glass microspheres and optionally hardener or catalyst for electrical conductivity and related applications especially for EM shielding. However, a shortcoming of this solution is that nano-structured carbon material (carbon nanotubes) reside within the matrix, but not on the surface of the spherical articles. Consequently the mitigation effect of the electromagnetic fields within the material is lower. Also the material does not contain reinforcement elements, which would grant mechanical toughness. Also the material does not include graphene - an effective component to capture the electromagnetic wave. Also, the material does not exhibit any 2D gradient properties in respect to density, particle size, composition, which is necessary to ensure an effective mechanism of internal reflections. Also, the invented material does not contain any metals or alloys coated spherical objects, that in combination with other types of conductive materials provide an effective EM mitigation effect against a wide frequency range.

The patent [13] discloses a graphene polymer composite material with network graphene. A corresponding preparation method comprises the steps of coating the surface of a polymer microsphere by the graphene, to obtain polymer/graphene composite particles; then pressing or pouring and moulding the obtained polymer/graphene composite particles, to obtain the graphene polymer composite material with the network graphene. However, one of the shortcomings of this solution is that, the material does not contain reinforcement
elements, which would grant mechanical toughness. Material does not contain matrix material, which would add to additional mechanical toughness of the material. Also, the material does not exhibit any 2D gradient properties in respect to density, particle size, composition, which is necessary to ensure an effective mechanism of internal reflections. Also, the invented material does not contain any metals or alloys coated spherical objects, that in combination with other types of conductive materials provide an effective EM mitigation effect against a wide frequency range. Additionally, the material requires a complex way of obtaining the graphene, using hazardous chemicals such as potassium permanganate, sodium nitrate, hydrogen peroxide, hydrochloric acid and hydrogen iodide acid and multistage synthesis process. The obtained composite material has weak mechanical properties, non resistant to organic solvents, high temperature and flames - due to organic material properties.

The patent [14] describes a foam material, preferably syntactic foam material which comprises of a matrix material, hollow bodies, preferably hollow spheres embedded in the matrix material, and particles influencing the properties of the foam material, preferably reinforcing particles which are arranged on the hollow bodies. However, the drawbacks of this solution are: according to this patent the largest dimension of the claimed structure does not exceed 1/500 from the maximal hollow bodies size of 900 microns: (1/500) x 900 microns = 1.80 microns, Also the material does not contain millimeter-scale composite rods that would reinforce the material and grant mechanical toughness. Another drawback of the invention is the arrangement of the reinforcement particles on the hollow body surface - the reinforcement is truly effective when positioned within the matrix material. Also, the patent does not describe including micro-sized rods and composite rods reinforcements. Also, the material does not exhibit any 2D/3D gradient properties in respect to density, particle size, composition, which is necessary to ensure an effective mechanism of internal reflections. Considering the small size of the reinforcement elements, and from the aspect of electromagnetic wave theory, since the wavelengths of the electromagnetic wave interact decisively differently with elements of larger size, hence the material has limitations within the electromagnetic frequency range. Additionally, the patent does not describe hollow bodies coated with single or multi-layered metal coating with insulator layer between them.

Carbon nanotubes (CNT) are an allotrope of carbon, one of the most promising exponents providing multifunctional reinforcements to the composite materials. These are
essentially long graphene tube-shaped material, having a diameter measuring on the nanometer scale, warped in different angles (chiral angles) and with different circumferential lengths (chiral vector), depending upon which they are able to offer a wide range of mechanical, electrical and thermal properties. However, none of the above described inventions have concentrated on exploiting the capabilities of CNT reinforced syntactic foams in the light of EM shielding requirements and prospective uses as lightweight multifunctional core materials in subsequent sandwich constructions designed for the same purpose.

Single-layer graphene demonstrated an excellent choice of material for high-performance EM shielding. CVD-synthesized graphene shows more than seven times greater EM shielding effectiveness (in terms of dB) than gold film of the same thickness. The ideal monolayer graphene can surprisingly shield as much as 98% of incident waves. CVD-synthesized graphene can shield up to 40%. It means that graphene is the most effective material for EM shielding in terms of shielding effectiveness per mass.

However, obtaining of graphene monolayer in centimetre scale is not simple task. At the same time nanostructures such as CNT, graphene flakes, uniform distribution in a viscous media such as polymer resin and ceramic slurry as well is not simple task. None of the above described inventions have concentrated on exploiting the capabilities of CNT and graphene deposited onto micro-scale material with further uniform distribution in matrix. The reinforced syntactic foams in the light of EM shielding requirements and prospective uses as lightweight multifunctional material.

The goal of the invention is to solve described above problems and other problems by distribution of graphene, CNT, NSMP on to micro scale spherical articles with subsequent distribution thereof in all material volume.

SUMMARY OF THE INVENTION

One aspect of the invention is a method of producing a composite shielding material in the form of a syntactic foam for shielding electromagnetic, acoustic and thermal emissions, said method comprising filling a mould with spherical or spherical-like articles made of ceramics, glass, or carbon, such articles coated with a layer of carbon nanostructures such as such as carbon nanotubes, graphene, graphene flakes and filling the voids between said
spherical-like articles in said mould with a matrix material, such as such as polymer resin, ceramic, glass, or metal-ceramic. The articles can be additionally covered with nano-sized metal or alloy particles and/or metal or alloy layer (with a thickness of 5-2000 nm, preferably 10-500 nm for metal particles and 5-2000 nm, preferably 5-500 nm for the single layer) metals such as iron, nickel, cobalt, chromium, tungsten, zinc, copper, silver, gold, platinum, palladium, rhodium, titanium, aluminium, magnesium, scandium, and/or their combination (as mixture of powders or alloys) deposited on the surface of the spherical articles. Metal alloys could be such as 316, 304, 41xx steels, AlSi27, AlSi70 or other. Nano-sized metal particles and/or metal or alloy layer could be coated with graphene layer. Spherical articles can have multiple metal layers separated by an insulating layer such as A l₂O₃, SiO₂, BN, SiC or other with a thickness of 5-2000 nm, preferably 3-300 nm. Additionally spherical articles could have multiple metal layers separated by the insulating layer such as A l₂O₃, SiO₂, BN, SiC or other with a thickness of 20-2000 nm, preferably 100-1000 nm. Additionally spherical articles could have multiple graphene/metal layers separated by the electric non-conductive material insulator such as A l₂O₃, SiO₂, BN, SiC or other with a thickness of 20-2000 nm, preferably 100-1000 nm. The metal layer is considered both a single type of metal layer and metal alloys layer. The composite material may additionally comprise of micro and/or nano-sized reinforcement elements mixed into the matrix material. Such composite material possesses both reflective and absorptive properties to improve shielding effectiveness. It can be used as shield against electromagnetic, acoustic, and thermal emissions.

The outer layer of the spherical or spherical like articles (SA) is defined as the layer which is most distant from the center of the SA. The inner layer of the SA is the layer towards the center of the SA starting from the outer layer.

Another aspect of the invention is a shielding composite material for protection people and equipment from the effects of electromagnetic, and acoustic emissions, comprising of the spherical or spherical-like articles encompassed by an organic or inorganic matrix material, said articles coated with carbon nanostructures (NS), nano-sized metal particles (NSMP), nanoscale layer(s) of inorganic isolator between graphene layers, matrix material, preferably reinforced by micro- and nano-sized structures.
Another aspect of the invention is a shielding composite material for protecting people and equipment from the effects of electromagnetic, acoustic, and thermal emissions, said material comprising spherical or spherical like articles (SA), made from ceramics, glass or carbon, said articles coated with carbon nanostructures (NS) such as graphene, graphene flakes, graphite, carbon nanotubes (CNT), and/or nano-sized metal particles (NSMP) such as iron, nickel, cobalt, chromium, copper, silver, gold, platinum, palladium, rhodium, titanium, and their combination (alloys). Additionally, articles can have nanoscale (3-300nm) layer(s) of inorganic insulator between graphene layers, such as alumina, silica, boron nitride, boron carbide. The articles are distributed within the matrix material such as polymer resin, ceramic, glass, or metal-ceramic, additionally reinforced with micro- and nano- sized rods (rods is a object with aspect ratio of length to diameter higher than 10. In case of transverse section differ from circle the diameter is a circle diameter where can be written the real transverse section), distributed in the matrix.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention can be better understood with reference to the following drawings- The drawings are not necessarily to scale, emphasis instead being placed upon clearly illustrating principles of the present invention.

Fig 1A depicts a composite material according to one embodiment of the invention
Fig 1B is a cross-section of the spherical article (SA) coated with graphene layers
Fig 2 depicts a material according to one embodiment of the invention
Fig 3A depicts a material according to another embodiment of the invention and Fig 3B is enlarged view of the material.

Fig 4 depicts a material according to yet another embodiment of the invention.
Fig 5 depicts a cross-section of the spherical article according to another embodiment.
Fig 6 depicts a cross-section of the spherical article according to another embodiment.
Fig 7 depicts a cross-section of the spherical article according to another embodiment.
Fig 8 depicts a cross-section of the spherical article according to another embodiment.
Fig 9 depicts a cross-section of the spherical article according to another embodiment.
Fig 10 depicts a cross-section of the spherical article according to another embodiment.

Fig 11 depicts a cross-section of the material by Scanning Electron Microscope (SEM) with magnification X 200 (a) and micro-computational tomography, magnification X 30 (b) images.

Fig 12 explains the meaning of gradient in this invention, in this particular case the gradient of material density.

Fig 13 is a planar representation of linear gradient.

Fig 14 is a planar representation of 2D sinusoidal gradient.

Fig 15 is an axonometric representation of 2D sinusoidal gradient.

Fig 16 is an axonometric representation of 3D sinusoidal gradient.

Fig 17 is an axonometric representation of 3D sinusoidal gradient single "tile" element (shown are two pieces).

Fig 18 is an axonometric representation of Pyramidal gradient single tile element.

Fig 19 is a schematic representation of surface made of 3D sinusoidal gradient elements.

Fig 20 is a schematic representation of surface made of pyramidal gradient elements.

Fig 21 is a schematic representation of 3D by complex formula gradient.

EXAMPLES OF CARRYING OUT THE INVENTION

The composite material 11 according to one embodiment is depicted in Fig 1A. The composite material comprises of spherical articles 3 of different sizes encompassed by the matrix material 5. Mould 4 is used to manufacture the composite material.

The material according to present invention is made of spherical or spherical-like articles (hereinafter spherical articles or SA) 3, for example as depicted in Fig 1B, wherein the surface 2 of the SA is coated with a layer 1 comprising carbon nanostructures (NS) such as graphene.
Said spherical articles are solid or hollow with wall thickness 5-20% from external diameter, and can be made of carbon, glass, as of pure alumina, silica, zirconia, boron nitride, tungsten carbide, silicone carbide as well of mixture of such materials in different proportions. Said SA can also be partially spherical, or having an elongated shape (ellipsoids with larger diameter D to smaller diameter d, e.g., from 1 to 10), or having otherwise non-regular shape. Said SA may be hollow or solid half sphere. Said spherical articles can be an agglomeration of two or more individual spherical articles.

Another embodiment of the material according to present invention is depicted in Fig 2. The material comprises of the SA 3 of different sizes encompassed by the matrix material 5. Mould 4 is used to manufacture the composite material. The embodiment as shown in Fig 2 also comprises of reinforcing micro rods 6, made of alumina, boron nitride or silicon carbide, tungsten, boron, or combination thereof. Rods are understood to have length to diameter ratio 10 or more. Such micro rods have diameter 20-300 μm and length 500-20000 μm. Such micro rods can be self-reinforced composite rods having inner rods made from tungsten wire with diameter 5-30 μm, and boron outer shell with thickness 40-150 μm, with diameter 100-200 μm and length 500-20000 μm added.

Matrix material 5 can be an organic matter such as: an epoxy, various polymers, silicone, rubber, ethylene propylene diene monomer (EPDM), fluorosilicone, polyoxypropylene POP), or inorganic: ceramics, glass and combination thereof, in a liquid condition (as slurry or molten in case of inorganic matrix material).

The matrix material may require curing, e.g., at room temperature for about 15-35 hours, or at elevated temperatures in the range of 80-180°C for about 1-5 hours and subsequent post curing at elevated temperatures in the range of 100-350°C for about 2-6 hours depending upon the system to form a syntactic foam.

Another embodiment is shown in Fig 3. The composite material comprises of the SA 3, micro rods 6, nanorods 7 (diameter 4-100 nm and length 50-10000 nm) encompassed by the matrix material 5. The nanorods are for reinforcement purposes. Mould 4 is used to manufacture the composite material. The nanorods also have length to diameter ratio 10 or more. The nanorods can be made from as pure alumina, silica, zirconia, boron nitride, silicone carbide as well of mixture of these, additionally nano-rods can be previously coated by graphene.
The distribution range $\eta$ of said spherical articles (SA) within the matrix material can be from 0.95 to 0.50, where $\eta = (\text{SA minimal diameter})/(\text{SA maximal diameter})$. In other words, the SAs can be relatively uniformly dimensioned. Alternatively, the SA distribution range $\eta$ can be between 0.5 to 0.001, i.e., the SAs can be substantially differently dimensioned.

The embodiment shown in Fig 4 has increasing distribution range $\eta$ growing up from one side of the composite material to the other side of the composite material, increasing from very low (e.g., 0.001) to very high (e.g., 0.95), resulting in gradient structure and thereby also in gradient properties of the material.

Fig 5 depicts another embodiment of the spherical article, where the surface 2 is etched to form extended surface 8 before graphene coating.

Fig 6 depicts yet another embodiment of the spherical article. The surface 2 of the spherical article 3 is coated with graphene layer 1, covered with nanoscale metal particles 9 such as iron, nickel, chromium, copper, silver, gold, platinum palladium, rhodium, titanium.

Fig 7 depicts another embodiment of the spherical article, where the extended surface 8 is coated by graphene layer 2 and subsequently decorated with metal nano particles 9.

Fig 8 depicts another embodiment of the spherical article where the surface 2 is coated with graphene layer 1 and carbon nanotubes 10.

Fig 9 depicts another embodiment of the spherical article, where the surface 2 is coated by graphene layer 1 and subsequently decorated with metal nano particles 9 and carbon nanotubes 10.

Fig 10 depicts yet another embodiment of the spherical article where the surface 2 is etched to form an etched surface 8 is, coated by graphene layer 1, and subsequently decorated with metal nano particles 9 and carbon nanotube 10.

Different methods can be used for coating the spherical articles, e.g., the graphene, graphite or carbon nanotubes layer can be deposited by chemical vapour deposition (CVD). Graphene flakes can be deposited by precipitation or spray coating.
Fig 11 is a cross section of material of Fig 1 by Scanning Electron Microscope with magnification X 200 (Fig 11a) and micro computational tomography, magnification X 30 (Fig 11b) images.

The method according to one embodiment of the invention includes the steps of filling a mould with spherical or spherical like articles, said articles coated with nanostructures such as carbon nano structures (NS) such as carbon nanotubes (CNT), graphene; and filling the mould with matrix material in liquid form.

According to one embodiment, during the filling of the mould 4 with spherical articles 3, additionally mould 4 vibration is used to evenly distribute the articles.

According to one embodiment, after filling the mould 4, with the spherical articles 3 the thermal or spark plasma sintering is used.

The present invention proposes the production of the syntactic foam material comprising of steps of depositing graphene layers on spherical articles (SA), filling the mould with graphene layer coated spherical articles (GCSA), filling the voids between the spherical articles with matrix material, such as organic matter, such as epoxy, various polymers, silicone, rubber, ethylene propylene diene monomer, fluoro silicone, poly oxypropylene, or inorganic matter such as ceramics, glass and combination thereof, in a liquid condition (as slurry or molten in case of inorganic matrix material).

During the filling of the mould with the matrix material, reduced pressure (in the mould) can additionally be used.

In case of matrix material has organic matter - curing at room temperature for about 15-35 hours, or at elevated temperatures in the range of 80-180° C. for about 1-5 hours and subsequent post curing at elevated temperatures in the range of 100-350° C. is used. For about 2-6 hours depending upon the system to form a syntactic foam. In case of self-hardening inorganic slurry curing can be carried out at 20-100°C for 50-100 hours, or 20-30°C for 5-15 days.

In all embodiments, the matrix material, with reinforcing nano-rods with diameter of 4-100 nm and length of 50-1000 nm are dispersed. The nano-rods can be made from pure alumina, silica, zirconia, boron nitride, silicone carbide as well of mixture of these, additionally nano-rods can be previously coated by graphene.
In all embodiments, the spherical articles can be solid or hollow with wall thickness of 5-20% from external diameter. The articles can be made of carbon, glass, as of pure alumina, silica, zirconia, boron nitride, silicon carbide as well of mixture of them.

In all embodiments, the spherical articles before graphene layer deposition can be coated with NSMP such as iron, nickel, chromium, copper, silver, gold, platinum palladium, rhodium, titanium.

In all embodiments, the SA distribution range \( \eta \) is from 0.99 to 0.01, where \( n=(\text{minimal average diameter of SA})/(\text{maximal average diameter of SA}) \). In some embodiments, the SA distribution range is from 0.99 to 0.5, i.e., the material is made of relatively uniform size articles. In some embodiments, the distribution range is from 0.01 to 0.5, i.e., the material is made of particles of substantially different sizes.

In all embodiments, the SA distribution range \( \eta \) can be substantially different in different areas of the material, e.g., across the cross section of the composite material, thereby providing composite materials with finely tuned absorption and reflective properties. For example, the distribution range \( \eta \) may be largest on one side of the composite material and smallest on the other side of the composite material (i.e., the distribution range \( \eta \) is growing up (from 0.01 to 0.95). The SA is filled into the mould, layer by layer, forming a material with gradient properties (gradient structure). Such structure is depicted in Fig 4. The distribution range \( \eta \) can also increase at the beginning and then decrease (or vice versa) across the cross section.

In all embodiments, the distribution range \( \eta \), type of coating can be also different in other directions of the composite materials and can change linearly, or according to predetermined formula (e.g., sin wave), i.e., can have a gradient, e.g., as described in Figs 12 to 21, or have different discrete values in different parts of the composite material.

Fig 12 shows the material with 1D gradient, where material properties (for example the density particle size, coating thickness or coating type) changes only by \( Z \) axis, but in each separate \( x-y \) layer is the same.

Fig 13 shows schematic interpretation of 1D gradient shown on Fig 12.

Fig 14 demonstrates 2D gradient material, where material properties change by \( x, y \) and \( z \) axis.
Fig 15 shows one layer of the 2D gradient material with equal properties. It has wave structure described by a single sinusoidal formula.

Fig 16 shows one layer of the 2D gradient with equal properties. It has wave structure described by double sinusoidal formula.

Fig 17 shows two pieces of tiles of 2D gradient material. To tiling by these elements is possible to obtain continuous surface of 2D gradient material with wave structure described by double sinusoidal formula shown on Fig 19.

Fig 18 is shown one piece of tiles of 2D gradient material. To tiling by these elements is possible obtain continuous surface of of 2D gradient material with a conic structure it is shown on Fig 20.

However, the material density can be changing throughout the material not only by linear law (the cone shown on Figs 18 and 19) or sinusoidal (the waves shown on Figs 15, 16, 17 and 19) but also according to another, more complex formulas (see, Fig 21).

The material according to the invention preferably comprises a mixture of articles of different type, wherein the composition of the mixture varies from one portion of the material to another portion of the material (e.g., from one layer to the other layer) at least in one direction of the material, thereby creating a material with changing properties in at least on direction, thereby forming a gradient structure. The different types of articles include:

- hollow or non-hollow spherical or spherical like articles made of ceramics, glass, or carbon, such articles coated with carbon nanostructures, such as carbon nanotubes, graphene, and graphene flakes;

- hollow or non-hollow spherical or spherical like articles made of ceramics, glass, or carbon coated with at least one metal layer, the metal layer preferably having thickness from about 10 to about 2000 nm;

- hollow or non-hollow spherical or spherical like articles made of ceramics, glass, or carbon has at least two layers of coating: outer coating of graphene, and bottom layer or layers of metal (or metals), said metal layer (or layers) preferably having thickness of 10 to about 2000 nm; and
- hollow or non-hollow spherical articles made of ceramics, glass, or carbon coated with two or more metal layers, preferably having thickness from about 10 to about 2000 nm, which are separated by a layer of insulating material.

The composition of the articles may include these different types of articles in any combination, having two or more types of articles in the mixture in any proportion. By varying the concentration of each types of articles from portion to portion of the material (e.g., from layer to layer through the cross section of the material) in at least one direction so that the material can have finely tuned electromagnetic and/or mechanical and/or sound absorption and reflective properties. For example, the content of the metal coated article may be highest on one side of the composite material and smallest on the other side of the material (i.e., the concentration is decreasing, e.g., from 95 vol% to 0 vol%) filled in the mould, layer by layer, forming a gradient structure. Such structure is depicted in Fig 12. The content of the metal coated SA can also first increase and then decrease (or vice versa) across the cross section of the material.

REFERENCES


[14] Stefan F. Foam material, preferably syntactic foam material comprises matrix material, hollow bodies embedded in matrix material, and particles influencing properties of foam material, preferably reinforcing particles arranged on hollow bodies. DE 102013007999 A1, 2012.
CLAIMS

1. A method of producing a composite shielding material in the form of a syntactic foam for shielding electromagnetic radiation (EMR), acoustic and thermal emissions, said method comprising of filling a mould with spherical or spherical-like articles made of ceramics, glass, or carbon, said articles coated on their external surface with carbon nanostructures, selected from the group consisting of carbon nanotubes, graphene and graphene flakes; and filling the voids between said articles with a matrix material.

2. A method as in claim 1, wherein said articles are coated with at least one metal layer.

3. A method as in claim 1 or 2, wherein said articles are coated with two or more metal layers, separated from each other by one or more layers, made of an insulating material.

4. A method as in claim 2, wherein said articles comprise at least one outer graphene layer on an inner metal layer.

5. A method as in claims 1 to 4, comprising additionally adding into the mould a second type of spherical or spherical-like articles made of ceramics, glass or carbon, said articles coated only with a metal layer on an external surface of the article of said second type.

6. A method as in claim 5, wherein said article of second type comprises of two or more metal layers separated from each other by one or more layers of insulating material.

7. A method as in claims 1 to 5, comprising filling the mould with at least two types of articles of ceramics, glass or carbon, said types selected from the group consisting of articles, said articles 1. coated with one metal layer; 2. coated with at least two metal layers, separated from each other by one or more layers of insulating material; 3. coated with a metal layer and a graphene layer on said metal layer; and coated with
one or more metal layers, one or more insulating layers between said metal layers, and a layer, comprising carbon nanotubes or carbon flakes.

8. A method as in claims 1-7, wherein said matrix material comprises of an organic material selected from a group consisting of epoxy, polymers, silicone, rubber, ethylene propylene diene monomer (EPDM), fluorosilicone, polyoxypropylene (POP).

9. A method as in claims 1-7, wherein said matrix material comprises of an inorganic material selected from a group consisting of ceramics, glass and metal-ceramic.

10. A method as in claims 1-9, wherein said matrix material is filled in a liquid state.

11. A method as in claims 1-10, comprising the step of creating a reduced pressure in said mould during filling the matrix material into said mould.

12. A method as in claims 1 to 11, comprising the step of curing and post-curing said matrix material in said mould.

13. A method as in claims 1 to 12, comprising the step of vibrating said mould during the step of filling said mould with spherical articles.

14. A method as in claims 1 to 13, comprising of applying electric, magnetic or electromagnetic field to the said mould during the step of filling with spherical articles, filling with matrix material and curing of matrix material.

15. A method as in claims 1 to 14, comprising the step of thermal sintering in vacuum, inert or reducing atmosphere after the step of filling said mould with spherical articles.

16. A method as in claims 1 to 15, comprising the step of spark plasma sintering after the step of filling said mould with spherical articles.
17. A method as in claims 1 to 16, comprising the step of dispersing micro rods with a
diameter about 20 to 300 µm and length from about 500 to about 20000 µm, into said
matrix material for reinforcement purposes.

18. A method as in claims 1 to 17, comprising the step of dispersing self-reinforced
composite rods, comprising an inner rods made of tungsten wire with a diameter from
about 5 to about 30 µm and a boron outer shell with a thickness from about 40 to
about 150 µm, and length from about 500 to 20000 µm, into said matrix material.

19. A method as in claims 1 to 18, comprising the step of dispersing nano-rods with a
diameter about 4 to about 100 nm and length about 50 to 10 000 nm, wherein the
nano-rods are made from pure alumina, silica, zirconia, boron nitride, silicon carbide,
or their mixtures or alloys, into said matrix material, for reinforcement purposes.

20. A method as in claim 19, wherein said nano-rods are previously coated with
graphene.

21. A method as in claims 1 to 20, wherein said articles are solid.

22. A method as in claims 1 to 20, wherein said articles are hollow with the wall
thickness of 5-20% with respect to the external diameter of said article.

23. A method as in claims 1 to 22, wherein said articles are coated with nano-sized metal
particles (NSMP) or layer(s) such as titanium, iron, nickel, chromium, copper, silver,
gold, platinum palladium, rhodium, or mixtures or alloys of such materials.

24. A method as in claims 1 to 23, wherein said articles are coated with carbon nanotubes
(CNT).

25. A method as in claim 24, wherein said articles are coated by CNT wherein after the
graphene layer is a nanoscale nonconductive insulator layer with thickness of about 3
to 300 nm.
26. A method as in claims 1 to 25, where said article has a distribution range \( \eta \) has a high value in the range from about 0.5 to 0.95, where \( n=(\text{minimal average diameter of SA})/(\text{maximal average diameter of SA}) \).

27. A method as in claim 1 to 25, wherein said article has a distribution range \( \eta \) has a low value from about 0.01 to about 0.5, where \( n=(\text{minimal average diameter of SA})/(\text{maximal average diameter of SA}) \).

28. A method as in claims 26 to 27, wherein said mould is filled layer by layer by alternating said \( \eta \) for each layer from said low value to said high value in at least in one the direction of the material, whereby a gradient structure of the material is formed.

29. A method as in claim 7 to 28, wherein said mould is filled layer by layer and articles are of two or more types and the concentration of each type of articles in each of said layers has different concentration, whereby a gradient structure in at least on direction of the material is formed.

30. A composite shielding material for shielding electromagnetic radiation, acoustic and thermal emissions, said material comprising a matrix material and spherical or spherical-like articles encompassed by said matrix material, said articles made of ceramics, glass or carbon, said articles coated with a layer of nanostructures, selected from the group consisting of graphene, graphene flakes and carbon nanotubes, or a combination thereof.

31. A material as in claim 30, wherein said articles includes articles that are coated with at least one metal layer.

32. A material as in claims 30 to 31, wherein said articles include articles that are coated with two or more metal layers, said metal layers separated from each other by one or more insulating layers.
33. A material as in claim 32, wherein said articles include articles that comprise of at least one outer graphene layer on an inner metal layer.

34. A material as in claims 30 to 33, comprising a second type of spherical or spherical-like articles made of ceramics, glass or carbon, said articles coated only with a metal layer on an external surface of the article of said second type.

35. A material as in claims 30 to 34, wherein said article of second type comprises of two or more metal layers separated from each other by one or more layers of an insulating material.

36. A material as in claims 30 to 35, wherein said material comprises of at least two types of articles of ceramics, glass or carbon, said types selected from the group consisting of articles, said articles 1. coated with one metal layer; 2. coated with at least two metal layers, separated from each other by one or more layers of insulating material; 3. coated with a metal layer and a graphene layer on said metal layer; and coated with one or more metal layers, one or more insulating layers between said metal layers, and a layer, comprising carbon nanotubes or carbon flakes.

37. A material as in claims 30 to 36, wherein said articles also comprises of a layer of nano-sized metal particles, wherein the voids between said coated spherical articles are filled with matrix material.

38. A material as in claim 41, wherein said metal is selected from a group consisting of aluminium, iron, nickel, cobalt, chromium, copper, silver, gold, platinum palladium, rhodium, titanium, their alloys and their combination.

39. A material as in claims 30 to 38, comprising of at least one nanoscale layer of inorganic insulator between said layers of nanostructures consisting of graphene.

40. A material as in claims 30 to 32, wherein the matrix material comprises of polymer resin, ceramic or metal-ceramic material, or glass.
41. A material as in claims 30 to 40, wherein said matrix material is reinforced with microsized rods, having aspect ratio of length to diameter higher than 10.

42. A material as in claims 30 to 41, wherein said matrix material is reinforced with nanosized rods, having aspect ratio of length to diameter higher than 10.

43. A material as in claims 30 to 42, where said articles have a distribution range $\eta$ has a high value in the range from about 0.5 to 0.95, where $n=(\text{minimal average diameter of SA})/(\text{maximal average diameter of SA})$.

44. A material as in claims 30 to 42, where said articles have a distribution range $\eta$ has a low value from about 0.01 to about 0.5, where $n=(\text{minimal average diameter of SA})/(\text{maximal average diameter of SA})$.

45. A material as in claims 43 to 44, wherein said material comprises of layers of articles, wherein said $\eta$ is alternated from said low value to said high value from one layer to the other in at least in one the direction of the material, whereby a gradient structure of the material is formed.

46. A material as in claims 36 to 45, wherein said material comprises of layers of mixture of articles, wherein the concentration of each type of articles varies from layer to layer, whereby the gradient structure is formed in at least one direction of the material.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08J9/32 B29C70/66 H05K9/00 H01B1/24

According to International Patent Classification (IPC) into both national classification and IPC

ADD.

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols):
C08J B29C H05K H01B

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

Electronic database consulted during the international search (name of data base and, where practicable, search terms used):
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>DE 10 2013 007999 AI (FUTURECARBON GMBH [DE]) 14 November 2013 (2013-11-14)</td>
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[ ] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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Date of the actual completion of the international search: 28 February 2017

Date of mailing of the international search report: 10/04/2017

Name and mailing address of the ISA:
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NL-2280 HV Rijswijk
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Authorized officer:
Mayer, Anne

Form PCT/ISA/210 (second sheet) (April 2005)
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