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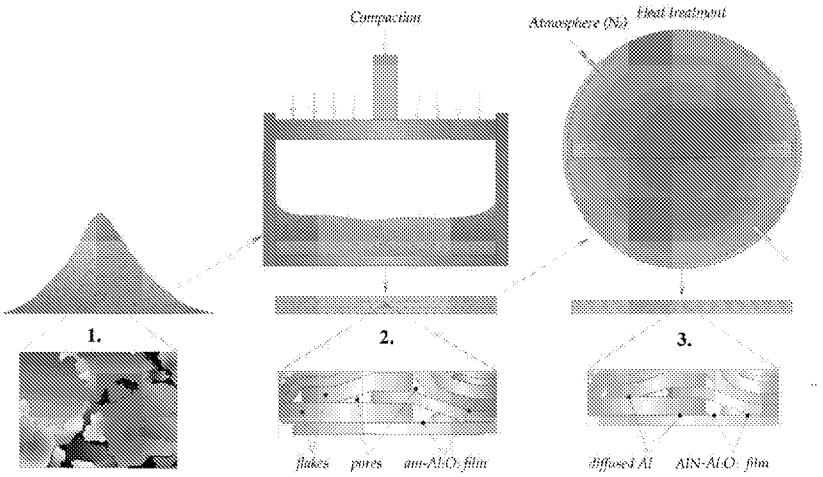


FIG. 1

(57) Abstract: A method for preparation of a phase change material aluminum composite including providing aluminum flakes and saturated fatty acid composition; inserting and compacting the composite into a mold; providing a compacted composite body of any shape, heating the compacted composite body; cooling the composite body to receive a porous composite; providing a phase change material; and infiltration of the provided phase change material into a pore of the porous composite.

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DESCRIPTION

LIGHTWEIGHT AND HIGHLY TOUGH ALUMINUM COMPOSITE WITH CERAMIC MATRIX

CROSS REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Provisional Patent Application Serial Nos. 62/496,256, filed October 12, 2016, and 62/604,304, filed July 3, 2017, the disclosure of each which is hereby incorporated by reference in its entirety, including any figures, tables, or drawings.

BACKGROUND

The economic and ecological benefits of using lighter but sufficiently rigid structures of aluminum foam (AF) in auto and railway industries are becoming more evident. Hollow aluminum (Al) alloy frames encased with an AF improve the structural integrity and crashworthiness of vehicles. Nevertheless, the specific energy absorption (ω) of open and closed-cell AFs even made of high-strength Al alloys (A306, A356, A206, and so forth) is limited to about 5 kJ/kg. Thus, current vehicles still largely rely on the mass and mechanical properties of the frames.

The prior art includes syntactic foams that suffer from relatively low specific toughness, and their fabrication and key differences are described below. Embodiments of the subject invention include a porous Al composite with an improved specific toughness.

Rohatgi (U.S. Patent US5899256) describes a method in which a syntactic Al foam is prepared through injection of liquid Al alloy (melt infiltration) through the adjoining microspherical shells of cenosphere fly ash. The method claims evacuation of a bed of cenospheres to a pressure below 40 kPa. As an example, the particle size is about 150 μm, with an infiltration time and temperature of 5 min and 800 °C, respectively. This technology and its various modifications can be economically sound, but often causes microstructural defects in Al composites. For example, inhomogeneous distribution of the microspheres, (e.g. < 100 μm), in the Al matrix can weaken the overall mechanical properties. The approach stipulated developing the powder metallurgy method, where Al alloy powder and the hollow microspheres are compacted together and sintered to provide reliable homogeneous structures.

Sherman and Doud (U.S. Patent No. US9096034) propose a conventional powder metallurgy technique, involving compaction of a mixture of alumina silicate microspheres (≈150 μm) with aluminum alloy powder (≈10 μm, A6061), and sintering in vacuum at about 500 °C. The principal claim is that before the compaction stage, the porous microspheres are additionally coated with aluminum using the chemical vapor deposition (CVD) method. Moreover, the powder mixture can be compressed numerous times, as in forging, to achieve thinner pores before the sintering stage. Meantime, the toughness of the disclosed example with a density of ≈2,000 kg/m^3 is about 30 kJ/kg out of a specific absorption capacity of about 138 kJ/kg.

An approach in aluminum powder metallurgy is the in-situ nitridation or reinforcement of compacted Al particles by stiff bonds of AlN. A syntactic Al foam can be prepared by using in-situ nitridation as described by Liu *et al.* (U.S. Patent No. US20100183471). For this purpose, Al6061 alloy macro particles are compacted with other metallic and ceramic powders and binders into a preform and are slowly (0.5-0.8 °C/min) heated in a nitrogen atmosphere to a temperature of up to 620 °C to form a reinforcing AlN skeleton. The method supposes further infiltration of the pre-fabricated composite by a molten Al alloy through the pores reinforced with AlN. Later, the authors describe a similar material, where the aluminum of the partially nitrided powder (12 hrs at 540 °C) is melted and vacuum withdrawn (2 hrs at 700 °C and 5 Pa) throughout the nitrided pores. As shown, this syntactic Al6061 foam contains small (5-20 μm) AlN shells uniformly dispersed within Al alloy matrix. This imparts the composite with improved deformability and a specific toughness of about 17 kJ/kg. However, the material processing is relatively complex and energy-intensive.

Schaffer *et al.* (U.S. Patent No. US5902943) carried out a nitriding procedure with a fine (> 44 μm) aluminum powder protected with stearic acid (0.1-2.0 wt%) and other known oxygen getters (Mg, Zn, Cu, and stearic acid) in a pure nitrogen gas. The radical nitriding appears after about ten elapsed minutes at the sintering conditions (raising the temperature at 10 °C/min to 600 – 630 °C). The preferable implementation of the invention recommends a heating rate in the range of 20-40 °C /min. As a result, rapid Al nitridation accumulates significant heat energy and controls the quick densification of the Al matrix. Nevertheless, a relatively large amount of the gained AlN drastically increases the composite strength but decreases its ductility. That is why such a brittle Al-AlN composite is unsuitable for impact absorption applications. It should be noted that the rapidly burned getters are key factors in

triggering the spontaneous growth of the AlN phase and densification of the composite structure at the moderate temperatures.

BRIEF SUMMARY

Embodiments of the subject invention describe methods for preparation through compaction of aluminum flakes into preforms and their extended heat treatment in a nitrogen atmosphere. The methods can include through additional processing such as infiltration by metals and polymers, polishing the material surface, painting, and other known secondary methods.

Embodiments of the subject invention provide methods of material preparation that include rapid heat treatment of aluminum flakes and porosity infiltration by using an appropriate phase change material. Additional processing such as polishing, painting, and other known methods can be further performed.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows an illustration of aluminum flakes transformed into a composite material. Three different states are shown: (1) aluminum flakes, (2) compacted aluminum flake powder, and (3) nitrided and sintered composite with the improved mechanical properties.

Figure 2 shows a plot of the boundary of annealing condition for preparation of the Al composites with improved mechanical properties.

Figure 3 shows plots of (a) compression stress-strain curves and (b) energy absorption characteristics of the samples of example 1.

Figure 4 shows plots of (a) compression stress-strain curves and (b) energy absorption characteristics of the samples of example 2.

Figure 5 shows plots of (a) compression stress-strain curves and (b) energy absorption characteristics of the samples of example 3.

Figure 6 shows an illustration of aluminum flakes transformed into the material for thermal energy storage applications. Three different states are depicted: (1) compacted aluminum flake powder, (2) rapidly annealed aluminum flake compact, and (3) PCM infiltrated composite.

Figure 7 shows micro images captured in the (a) center and the (b) near edge zone in the rapidly annealed composite. The sample porosity is about 22%.

Figure 8 shows plots of (a) bulk density and (b) specific heat capacity of the rapidly annealed composites with empty (1) and CtO infiltrated (2) pores.

Figure 9 shows plots of an effect of the porosity or PCM volume fraction on the (a) thermal diffusivity and (b) conductivity in the rapidly annealed composite material.

Figure 10 shows the exterior surfaces of the Al composite (Ex. 10, see Table 1) before and after the fire test.

DETAILED DESCRIPTION

As used herein, the term 'Al flakes' is meant to indicate flattened Al or Al alloy structures with a thickness in a range of above 40 nm and below 500 nm.

As used herein, the term 'getter' or 'oxygen getter' is intended to indicate an organic or inorganic compound which effectively deoxidizes nitrogen gas at elevated temperatures.

As used herein, nitridation-driven diffusion indicates aluminum spreading out of Al flakes due to highly exothermal nitridation of Al and oxidation of a getter.

As used herein, partial nitridation is intended to indicate a chemical reaction between Al and N_2, which is triggered by the rapid burning of a getter spread on Al flakes.

Embodiments of the subject invention provide preparation methods for a lightweight aluminum composite with a unique structure, allowing improved formability, strength, deformability, specific toughness, and specific energy absorption capacity. These properties can be attributed to a pile-oriented structure assembled from aluminum flakes bonded by partial nitridation and the nitridation-driven diffusion of aluminum.

Certain embodiments use aluminum flakes with a specific surface area from 3 m^2/g to 15 m^2/g. The Al flakes can include an oxygen getter of less than 5 wt%. The aluminum flakes can be compacted using a pressure ranging from about 60 MPa to about 500 MPa to obtain an Al flake compact with a density of about 2,200 kg/m^3 to about 1,300 kg/m^3, respectively. The compaction of the flakes can be carried out through isostatic pressing, forging, extrusion or other molding techniques in the temperature range from about 20°C to about 80°C. The Al compact represents a relatively brittle, but durable material for further processing stages. Then, the compact can be heated to a temperature from 500 to 600°C in a nitrogen atmosphere (N_2 > 90%). The heat treatment stage can start from a rapid heating (for

example, 20-50°C/min) of the powder compact to the annealing temperature, where it can remain for a period between 1 and 720 min.

The rapidly burned getter can trigger spontaneous Al nitridation in between the joint flakes and form reinforcing pore channels in the Al compact. At the same time, the heat of nitridation and getter burning can facilitate diffusion of the aluminum out of the flakes throughout the formed AlN pore channels. The optimization of Al nitridation and diffusion delivers a lightweight Al composite with improved mechanical properties, such as the specific toughness and specific absorption capacity. As partially described herein, the preparation method does not limit the claimed matter. For example, some embodiments of the annealed composite have an open porosity, through which the annealed composite can be infiltrated with molten polymers, metal alloys, or phase change materials to improve the mechanical and functional properties. The properties of prepared Al composites can also be enhanced through using the standard precipitation hardening methods, which can increase the yield strength of the aluminum flakes or the annealed flake composite.

The density of the annealed flake composite can range from about 1,400 to 2,600 kg/m^3, and the specific toughness and absorption capacity of the composite can lie in the range of 5-60 kJ/kg and 10-95 kJ/kg, respectively. The energy absorption characteristics are given by a few examples to indicate the potential of the claimed matter, rather than its limits.

Certain embodiments of the subject invention describe methods for preparation through compaction of aluminum flakes into preforms and their extended heat treatment in a nitrogen atmosphere, as seen in Figure 1. The method can include additional processing such as infiltration by metals and polymers, polishing the material surface, painting, and other secondary methods.

A preparation method according to a certain embodiment can include the following four steps: step 1, can be providing the aluminum flakes representing aluminum or aluminum alloy in a precipitation hardened state, partially coated with a fatty acid composition; step 2, can be providing a preform of any shape, consisting of or comprising the aluminum flakes and additive powders such as metals (Al, Ti, Mg, Ni, Cu, Sn, Zr, Zn, Sc, Fe, Si, Pb, or V), and their carbides, nitrides, or borides; step 3, can be heating and annealing of the preform; and step 4, can be cooling of the annealed preform to receive the porous Al composite.

In step 1, the aluminum flakes can be a relatively pure (99.5% min) compound or alloy with the following additives: Cu, Fe, Si, Zn, Ni, Mn, Mg, Ge, Ti, Pb, Zr, or V. The average thickness of the Al flakes can be in the range from about 40 to about 500 nm. In

certain embodiments the aluminum based powder has an average thickness from about 80 nm to 10000 nm. The other dimensions of the flakes can be in any size from 40 nm to 1 mm. The powder size distributions in the specified range do not distort the desired implementation of the invention. The fraction of fatty acid getter can vary from 0.3 to 5 wt% in the Al flake composition and can be an important aspect in triggering nitridation and bonding of the Al flakes during the heat processing.

In step 2, the aluminum flakes can be mixed with one or more of the following additives: metals (Al, Ti, Mg, Ni, Cu, Sn, Zr, Zn, Sc, Fe, Si, Pb, or V), and their carbides, nitrides, or borides to get a powder composition. The additives are in near round shape with a size ranging from 50 nm to 1 mm.

The powder composition can be stirred by agitating vanes to get a free flowing powder. This powder can be then fed into a mold (or extruder) and compressed in a pressure range from about 60 to about 500 MPa. The powder composition can be repeatedly compressed to obtain a density of not less than 1,200 kg/m^3 and not more than 2,200 kg/m^3. Apart from the isostatic compaction, the powder composition can be extruded for shaping into long-span objects of a fixed cross-section profile. In some embodiments, the aluminum flakes can be 3D printed into a compact with specific dimensions.

In step 3, the powder preform can be moved into a heating furnace with a flowing atmosphere of nitrogen. The nitrogen purity can be from 90 to 99.9999%. The heating furnace can be sealed or semi-open with a material delivering conveyor. The heating furnace ensures rapid heating of the powder preform to a temperature of up to 600°C. The heating rate can be in a range of 5-100 °C /min. The gas flow rate can be varied from 10 to 10000 ml/min. In the case of a semi-open furnace, the appropriate heating can be controlled by the conveyor belt speed. Once the preform reaches the set temperature, the annealing duration lasts for not more than 720 min. A deviation from the heating conditions can impair the material structure and the mechanical properties. In many cases, the toughness can be decreased due to the AlN skeleton overgrowing within the particles.

In step 4, the annealed preform can be cooled down to a particular temperature below 50°C. In addition, the annealed composite can be toughened by using standard precipitation hardening methods.

Compared to AFs, typical syntatic aluminum foams (SAFs) where an Al alloy matrix encircles closely packed ceramic balloons (100-500 μm Al_2O_3, or 15-175 μm Al_2O_3-SiO_2), are more efficient ($\omega \approx$ 20-50 kJ/kg) in the absorption of impact energy. Although typical

SAFs can have greater compression strength (40-350 MPa), they are semi-brittle and fracture at a strain of below 5%. As a result to the specific toughness, σ_T, of these SAFs, the energy absorption up to the material fracture is 3-5 kJ/kg. A smaller size of the ceramic balloons, (for example, $\ll$ 100 μm), can improve the fracture strain and toughness. However, smaller size of the ceramic microballoons can technologically limit conventional SAF production, for instance injection of liquid Al alloy, (~730 °C) through the adjoining ceramic balloons. The liquid aluminium does not wet the alumina surface up to 880 °C and it hinders adhesion of Al to the microballoons with a developed surface area. As a result, the maximum shear strength between Al and Al_2O_3 is about 40 MPa. However, in a perspective bi-matrix SAF, liquid A6061 alloy strongly wets a porous AlN skeleton of 5-20 μm hollows at about 700 °C. This SAF fractures at a stress and strain of about 200 MPa and 17%, which is equal to a specific toughness of 14 kJ/kg. Without the alloy matrix, the porous skeleton remains brittle, especially with a greater volume of AlN. Furthermore, syntactic foams with only an aluminum matrix can be vulnerable to fire. A potential solution can be to use heavier composites with a steel matrix or ceramic matrix.

In certain embodiments, using hollow ceramic (Al_2O_3, SiO_2, SiC, and their composition) balloons or spheres with the diameter size ranging from 50 to 1000 μm can be utilized. For example, the balloons can be coated with a thin layer of aluminum for providing better adhesion to the aluminum flakes in the powder composition. The flakes and the balloons can be uniformly mixed and compressed into a porous compact with a particular porosity. Then, the compacted mixture can be heat treated under the conditions as given in fabrication step 3.

A rapid heat treatment can be implemented by using an induction heating process as aluminum flakes are electrically conductive media. For this case, continuous compacts (rods, bars, profiles, etc.) can be put into a tube (carbon, quartz, alumina, glass, or other ceramic material) for the containment of the gaseous atmospheres. Further, the tube can be continuously passed through the induction coil generating the Joule heat in the encased compacts).

The nitrogen atmosphere can be replaced by other common gases or vacuum. For example, the heat treatment stage can be as follows: annealing in the flowing nitrogen atmosphere changed by argon, hydrogen, ammonia gases, or vacuuming. The annealing in

the other gases or vacuum can last from 1 min to 720 min. The purity of the replacing gases can be from 90 to 99.9999%.

Certain porous embodiments of the annealed composite can be improved by partial or complete infiltrating of its structure with liquid metal alloys on the base of Mg or Al, or polymers (UHMW polyethene, poly(methyl methacrylate), epoxy, and other similar reinforcing polymers.

In certain embodiments material preparation includes slight sintering of the preforms followed by open porosity infiltration with an appropriate phase change material. Additional processing such as polishing, painting, and other methods do not limit the composites.

In certain embodiments, a preparation method for the composite embodiment can involve the following steps: step 1 can be providing aluminum or aluminum alloy in a flake state, coated with a saturated fatty acid composition; step 2 can be providing a compacted composite body of any shape, where the body comprises the aluminum flakes; step 3 can be rapid annealing of the compacted composite body; step 4 can be cooling the partially sintered body to receive the porous composite; step 5 can be providing a PCM mostly based on fatty acid entities; and step 6 can be infiltration of the provided PCM into the composite pore channels.

In step 1, the aluminum powder can be a relatively pure (99.5% min) compound or alloy with the following additives: Cu, Fe, Si, Zn, Ni, Mn, Mg, Ge, Ti, Pb, or Zr. The aluminum powder can be of any particle length distribution averaging from about 100 nm to about 1 mm.- The powder size distributions in the specified range do not distort the desirable implementation of the invention. The average aluminum flake thickness can be from about 40 to 500 nm. The saturated FA fraction can vary from 0.3 to 5 wt% in the Al flake composition to avoid unnecessary oxidation of the compacted Al flakes during the heat processing.

In certain embodiments, step 1 can include, providing aluminum (99.5% min) in a powder state or aluminum alloys classified from the 2xxx to 9xxx series. Aluminum flakes can have the length distribution ranging from about 100 nm to about 1 mm. The aluminum powder can contain at least 0.3 wt% and not more than 5 wt% of saturated fatty acid as the getter.

In step 2, the powder composition can be stirred by agitating vanes to get a free flowing powder. This powder can be then fed into a mold (or extruder) and compressed in a pressure range from about 70 to about 310 MPa. The powder can repeatedly be compressed

to obtain a density not less than 1,300 kg/m^3 and not more than 2,200 kg/m^3. Apart from the isostatic compaction, the aluminum flakes can be extruded for shaping into long-span objects of a fixed cross-section profile.

In step 3, the compacted powder moves into a heating chamber with a flowing gas of nitrogen with a purity of above 90%. The heating furnace can be sealed or semi-open with a material delivering conveyor. The heating furnace should ensure rapid heating of the powder compact to a temperature of about 500-600 °C. The heating rate to the annealing temperature can be in a range of 5-100 °C/min. In the case of a semi-open furnace, the appropriate heating can be controlled by the conveyor belt speed. Once the material reaches the set temperature, the annealing duration lasts for not more than 720 min.

In certain embodiments, the nitrogen-containing atmosphere comprises at least 95% nitrogen and the remaining 5% of H_2O, NH_3, and O_2, in any proportion thereof.

In step 4, the partially sintered aluminum particles rapidly (>40 °C/min) cool down to a particular temperature below 50°C. The quick cooling can prevent unwanted oxidation of the aluminum surface.

In step 5, an organic PCM mainly (greater than or equal to 70%) composed of saturated fatty acids in various proportions can be provided. The proportion depends on the PCM melting point needed for particular conditions of the TES application. In certain embodiments, a PCM includes regular coconut oil.

In step 6, the selected PCM can be directly infiltrated into the porous aluminum composite. Primarily, the selected PCM can be heated to a temperature that can be 3-4 times higher than the PCM melting point. Secondly, the porous composite can be immersed into the PCM and incubated for a period from 1 to 12 hr(s). An alternative infiltration method can be by vacuum infiltration, where conditions evacuate the porous body and let the hot PCM infiltrate the pore channels. PCM can fill up of the porous material in a few minutes. In certain embodiments, PCM can fill the pores of the aluminum body with the aid of evacuation of the pore channels at pressures from 10 to 100 Pa. In other embodiments, PCM fills the pores of the aluminum body with the aid of ultrasonication.

In certain embodiments, the composite can be cut, polished, laminated, and painted.

The subject invention includes, but is not limited to, the following exemplified embodiments.

Embodiment 1. A method for preparation of a phase change material-aluminum composite, the method comprising:

providing aluminum flakes coated with a saturated fatty acid composition;

inserting and compacting the aluminum flakes into a mold;

providing a compacted composite body of any shape;

heating the compacted composite body;

cooling the composite body to receive a porous composite;

providing a phase change material (PCM) including a saturated fatty acid; and

effecting infiltration of the provided PCM into a pore of the porous composite.

Embodiment 2. The method according to embodiment 1, in which the aluminum flakes have a length distribution of 100 to 1,000,000 nm.

Embodiment 3. The method according to any of embodiments 1-2, in which the aluminum flakes have a thickness of about 80 to 300 nm.

Embodiment 4. The method according to any of embodiments 1-3, in which, the aluminum flakes contain at least 0.3 wt% and not more than 5 wt% of the saturated fatty acid.

Embodiment 5. The method according to any of embodiments 1-4, in which the aluminum flakes are compacted to obtain a density of not less than 1,200 kg/m^3 and not more than 2,200 kg/m^3.

Embodiment 6. The method according to any of embodiments 1-5, in which the compacted composite body is heated in a heating chamber with a flowing nitrogen gas,

in which the nitrogen-containing atmosphere in the chamber comprises at least 95% nitrogen and the remaining 5% of H_2O, NH_3, and O_2, in any proportion thereof.

Embodiment 7. The method according to any of embodiments 1-6, in which the compacted composite body is cooled at a rate of greater than 40 °C/min to a temperature below 50°C.

Embodiment 8. The method according to any of embodiments 1-7, in which the PCM infiltrates the pores of the composite body with the aid of evacuation of the pores at pressures from 10 to 100 Pa.

Embodiment 9. The method according to any of embodiments 1-8, in which the PCM infiltrates the pores of the composite body by heating the PCM to a temperature that is 3-4 times higher than a melting point of the PCM and immersing the composite body into the PCM for a period from 1 to 12 hr(s).

Embodiment 10. The method according to any of embodiments 1-9, in which the PCM includes at least 70% saturated fatty acids.

Embodiment 11. A method for preparation of an aluminum based composite body with a ceramic matrix, the method comprising:

providing aluminum flakes partially coated with a fatty acid composition;

inserting and compacting the aluminum flakes in a mold;

providing a preform of any shape, consisting of the aluminum flakes;

heating and annealing of the preform; and

cooling of the annealed preform to receive a porous aluminum composite.

Embodiment 12. The method according to embodiment 11, further comprising:

heating the preform in a heating chamber with a flowing nitrogen gas; and

cooling of the annealed preform to receive an aluminum composite with an aluminum nitride (AlN) matrix.

Embodiment 13. The method according to any of embodiments 11-12, in which the aluminum flakes include the following: Cu, Fe, Si, Zn, Ni, Mn, Mg, Ge, Ti, Pb, Zr, V, or carbides, nitrides, or borides thereof.

Embodiment 14. The method according to any of embodiments 11-13, in which a fraction of fatty acid composition can be in a range of 0.3 to 5 wt%.

Embodiment 15. The method according to any of embodiments 11-14, in which the aluminum flakes and the fatty acid composition are compacted to obtain a density of not less than 1,200 kg/m^3 and not more than 2,200 kg/m^3.

Embodiment 16. The method according to any of embodiments 11-15, in which the preform is heated in a heating furnace, in which a temperature in the heating furnace is in a range of 500- 600 °C.

Embodiment 17. The method according to any of embodiments 11-16, further comprising

providing hollow ceramic spheres;

mixing and compacting the hollow ceramic spheres and aluminum flakes;

providing a preform of any shape, comprising the aluminum flakes and hollow ceramic spheres; and

cooling of the annealed preform to receive a porous composite.

Embodiment 18. The method according to embodiment 17, in which the hollow ceramic spheres include Al_2O_3, SiO_2, SiC, or a combination thereof.

Embodiment 19. The method according to any of embodiments 17-18, in which the hollow ceramic spheres have a diameter size ranging from 50 to 1000 μm.

Embodiment 20. The method according to any of embodiments 17-19, further comprising:

infiltration of the porous composite with Mg, Al, ultra high molecular weight polyethene, poly(methyl methacrylate), epoxy, or other reinforcing polymers.

All patents, patent applications, provisional applications, and publications referred to or cited herein are incorporated by reference in their entirety, including all figures and tables, to the extent they are not inconsistent with the explicit teachings of this specification.

Following are examples that illustrate procedures for practicing the invention. These examples should not be construed as limiting. All percentages are by weight and all solvent mixture proportions are by volume unless otherwise noted.

EXAMPLE 1

A group of samples is produced at a boundary of claimed annealing conditions as seen in Figure 2. The preparation method of example 1 involves the following steps: step 1, providing the aluminum flake powder with an average thickness of about 70 nm and a specific surface area of about 10 m^2/g. The Al flakes contain approximately 1.5 wt% of stearic fatty acid; step 2, agitating of the aluminum flakes followed by cold isostatic compaction at a pressure of about 70-380 MPa into the preform with a porosity of 25 - 50%; step 3, heating of the powder preform up to 520 °C at a rate of 20 °C/min, where nitrogen gas of 99.95% purity serves as the flowing atmosphere. Upon reaching the annealing temperature, the material rests at the annealing temperature for 30 minutes; and step 4, cooling the annealed preform at a rate of 20 °C/min to about 25 °C.

Quasi-static compression testing was conducted following ISO13314 on cylindrical samples with the nearly equal diameters and thicknesses, 9.2-10.0 mm. The test was performed using an 810 Material Testing System (MTS Systems Corporation, USA) with a self-leveling plate, evenly loaded at an initial strain rate of ~10^{-3} 1/s. The top and bottom surfaces of each specimen were polished to achieve better parallelism. The energy absorption capacity (J/m^3) can be the work of compression per unit volume and can be calculated as the area under the compressive stress-strain $\sigma(\varepsilon)$ curve:

$$U = \int_0^{\varepsilon} \sigma(\varepsilon) d\varepsilon \qquad (1)$$

where σ (MPa) and ε (cm cm^{-1}) are the compressive stress and strain, respectively. In this case, the strain ε ranges until the densification level, where $\varepsilon = e_2$.

In the case of the toughness, the energy can be absorbed until structure fracture, which occurs at a first maximum e_1 in the domain ε.

The specific energy absorption capacity and specific toughness are the values per unit weight, and are calculated as follows:

$$u = U d^{-1} \qquad (2)$$

where d is the density of the composite.

Figure 3a shows the quasistatic compressive stress-strain curves of the samples of example 1. Figure 3b indicates the results of the specific toughness and absorption capacity for the samples of example 1.

EXAMPLE 2

A group of samples is produced at the other boundary of the claimed annealing conditions. The preparation method of example 2 can be essentially the same as example 1 and differs only in step 3, employing an annealing temperature of about 580°C and an annealing time of about 420 min.

Figure 4a shows the quasistatic compressive stress-strain curves of the samples of example 2. Figure 4b indicates the results of the specific toughness and absorption capacity for the samples of example 2.

EXAMPLE 3

A group of samples is produced at the other boundary of claimed annealing conditions. The preparation method of example 3 can be essentially the same as example 1 and differs only in step 3, employing an annealing temperature of about 560°C and an annealing time of about 240 min.

Figure 5a shows the quasistatic compressive stress-strain curves of the samples of example 3. Figure 5b indicates the results of the specific toughness and absorption capacity for the samples of example 3.

EXAMPLE 4

Example 4 represents the lightest composite with minimum thermal conductivity, but highest heat storage capacity. The preparation method of Example 4 involves the following steps: step 1, providing the aluminum flake powder with an average thickness of about 60 nm and the following impurities: O_2 (~1.5 wt%), Pb (< 0.03 wt%). The getter represents stearic fatty acid at an amount of approximately 1.5 wt%; step 2, agitating of the aluminum flakes followed by cold isostatic compaction at a pressure of about 70 MPa into the compacts with a porosity of about 47%; step 3, heating the compacted powder specimens up to 600°C at a rate of 40 °C/min, where a nitrogen gas of 99.5% purity, O_2 of 50 ppm and H_2O of 50 ppm served

as the flowing atmosphere. Upon reaching the annealing temperature, the material rests in the furnace for one minute; step 4, cooling the sintered material at a fast rate of 40 °C/min to about 25°C, step 5, providing non-RBD coconut oil with about 94% of saturated fatty acids; and step 6, direct infiltrating the PCM into the specimen through the immersing-storing process, taking 1 hour.

The porosity of the annealed composite is about 47%. Figures 8, 9, show key properties of the prepared composite case.

EXAMPLE 5

Example 5 represents the densest composite with maximum thermal conductivity, but lowest heat storage capacity. The preparation method of Example 5 can be essentially the same as Example 4 and differs only in step 3, employing cold isostatic compaction of the flakes at a pressure of about 310 MPa to obtain a compact with a porosity of about 22%. The porosity of the annealed composite is about 22%.

Figures 8, 9 show key properties of the prepared composite case.

EXAMPLES 6-9

Besides the boundary cases, the intermediate results in Figures.8, 9 characterise the other examples (Examples 6 to 9), which differ in step 3 and were compacted to the following approximate porosities: 26, 32, 38, 42%, respectively. The porosity of the annealed composites is about 26, 32, 38 and 42%, respectively.

EXAMPLES 10,11

For the test for fire resistance, the composite samples were fabricated according to Embodiments 14-20, in the shape of cylindrical samples with a thickness and diameter of about 4 mm and about 28 mm, respectively. Two samples with different porosities were put into an electrically heated chamber furnace (Nabertherm N11/H 1280), rapidly (20 °C /min) heated to 1000°C and remained for 90 minutes. Table 1 shows the influence of the test conditions on the geometry and mass changes due to Al oxidation. The visual observation showed no sign of material deformation during the fire test. As measured, the material volumes increased insignificantly, below 3%.

Table 1. The effect of the fire test on the change of volume, mass and density of the composite

Ex. No	AlN matrix volume	Density (before)	Volume increase	Mass increase	Density (after)
	vol%	kg/m^3	vol%	wt%	kg/m^3
10	32	2,100	2.5	4.2	2,133
11	40	1,633	0.4	10.7	1,800

Over the testing, the sample (Example 10) surface changes the morphology (see, for example, Figure 10). However, slight polishing removes the stain out of the surface. Thus, the visual appearance of the material can retain its luminous properties after the fire exposure.

It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application and the scope of the appended claims. In addition, any elements or limitations of any invention or embodiment thereof disclosed herein can be combined with any and/or all other elements or limitations (individually or in any combination) or any other invention or embodiment thereof disclosed herein, and all such combinations are contemplated with the scope of the invention without limitation thereto.

CLAIMS

What is claimed is:

1. A method for preparation of a phase change material-aluminum composite, the method comprising:

providing aluminum flakes coated with a saturated fatty acid composition;

inserting and compacting the aluminum flakes into a mold;

providing a compacted composite body of any shape;

heating the compacted composite body;

cooling the composite body to receive a porous composite;

providing a phase change material (PCM) including a saturated fatty acid; and

effecting infiltration of the provided PCM into a pore of the porous composite.

2. The method of claim 1, in which the aluminum flakes have a length distribution of 100 to 1,000,000 nm.

3. The method of claim 1, in which the aluminum flakes have a thickness of about 80 to 300 nm.

4. The method of claim 1, in which the aluminum flakes contain at least 0.3 wt% and not more than 5 wt% of the saturated fatty acid.

5. The method of claim 1, in which the aluminum flakes are compacted to obtain a density of not less than 1,200 kg/m^3 and not more than 2,200 kg/m^3.

6. The method of claim 1, in which the compacted composite body is heated in a heating chamber with a flowing nitrogen gas, and

in which the nitrogen-containing atmosphere in the chamber comprises at least 95% nitrogen and the remaining 5% of H_2O, NH_3, and O_2, in any proportion thereof.

7. The method of claim 1, in which the compacted composite body is cooled at a rate of greater than 40 °C/min to a temperature below 50°C.

8. The method of claim 1, in which the PCM infiltrates the pores of the composite body with the aid of evacuation of the pores at pressures from 10 to 100 Pa.

9. The method of claim 1, in which the PCM infiltrates the pores of the composite body by heating the PCM to a temperature that is 3-4 times higher than a melting point of the PCM and immersing the composite body into the PCM for a period from 1 to 12 hr(s).

10. The method of claim 1, in which the PCM includes at least 70% saturated fatty acids.

11. A method for preparation of an aluminum based composite body with a ceramic matrix, the method comprising:

providing aluminum flakes partially coated with a fatty acid composition;

inserting and compacting the aluminum flakes in a mold;

providing a preform of any shape, comprising the aluminum flakes;

heating and annealing of the preform; and

cooling of the annealed preform to receive a porous aluminum composite.

12. The method of claim 11, further comprising:

heating the preform in a heating chamber with a flowing nitrogen gas; and

cooling of the annealed preform to receive an aluminum composite with an aluminum nitride (AlN) matrix.

13. The method of claim 11, in which the aluminum flakes include the following: Cu, Fe, Si, Zn, Ni, Mn, Mg, Ge, Ti, Pb, Zr, V, or carbides, nitrides, or borides thereof.

14. The method of claim 11, in which a fraction of fatty acid composition is in a range of 0.3 to 5 wt%.

15. The method of claim 11, in which the aluminum flakes and the fatty acid composition are compacted to obtain a density of not less than 1,200 kg/m^3 and not more than 2,200 kg/m^3.

16. The method of claim 11, in which the preform is heated in a heating furnace, in which a temperature in the heating furnace is in a range of 500- 600 °C.

17. The method of claim 11, further comprising

providing hollow ceramic spheres;

mixing and compacting the hollow ceramic spheres and aluminum flakes;

providing a preform of any shape, comprising the aluminum flakes and hollow ceramic spheres; and

cooling of the annealed preform to receive a porous composite.

18. The method of claim 17, in which the hollow ceramic spheres include Al_2O_3, SiO_2, SiC, or a combination thereof.

19. The method of claim 17, in which the hollow ceramic spheres have a diameter size ranging from 50 to 1000 μm.

20. The method of claim 17, further comprising:

infiltration of the porous composite with Mg, Al, ultra high molecular weight polyethene, poly(methyl methacrylate), epoxy, or other reinforcing polymers.

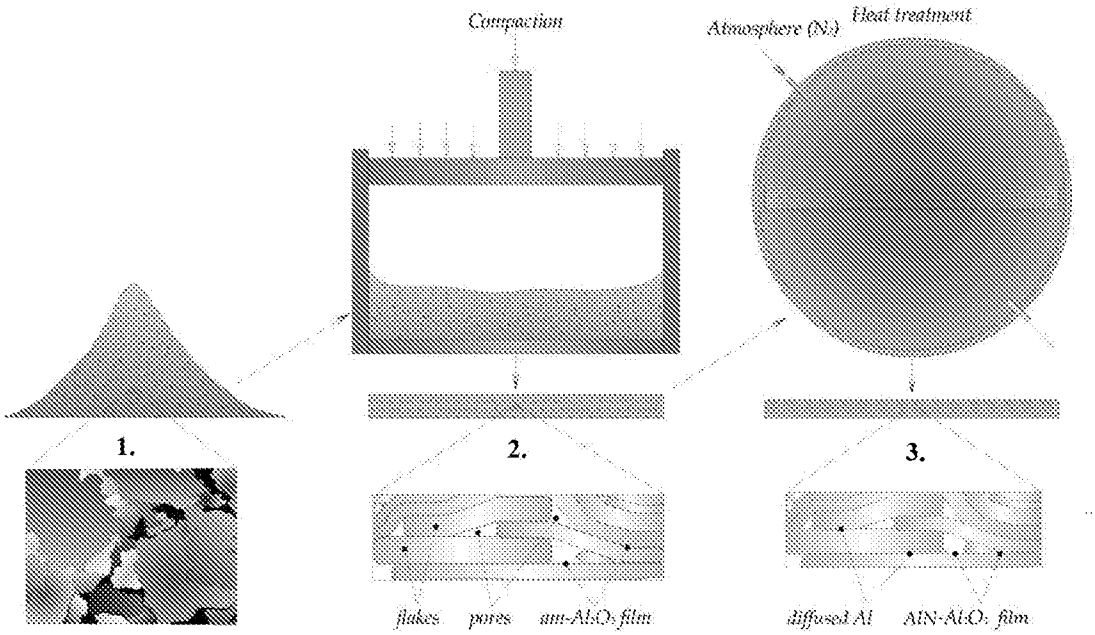

Compaction
Atmosphere (N_2)
Heat treatment
1.
2.
3.
flakes
pores
am-Al_2O_3 film
diffused Al
AlN-Al_2O_3 film

FIG.1

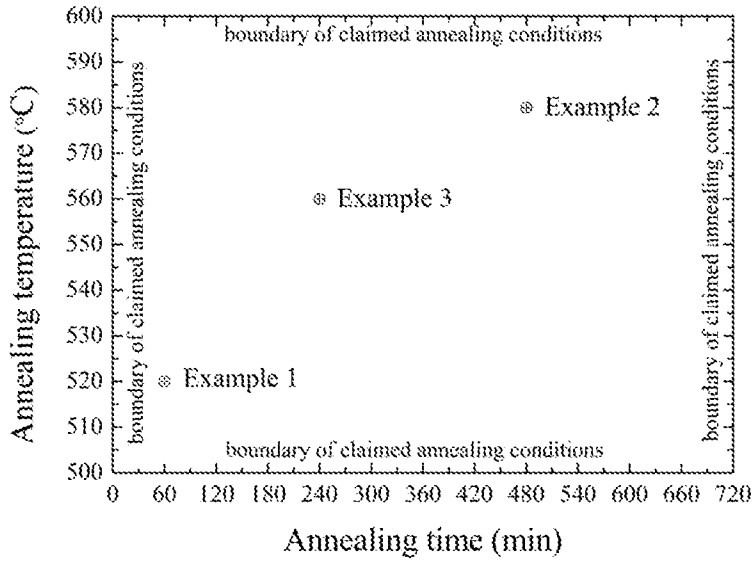

boundary of claimed annealing conditions
boundary of claimed annealing conditions
boundary of claimed annealing conditions
boundary of claimed annealing conditions
Example 1
Example 2
Example 3
Annealing temperature (°C)
Annealing time (min)
600
590
580
570
560
550
540
530
520
510
500
0
60
120
180
240
300
360
420
480
540
600
660
720

FIG.2

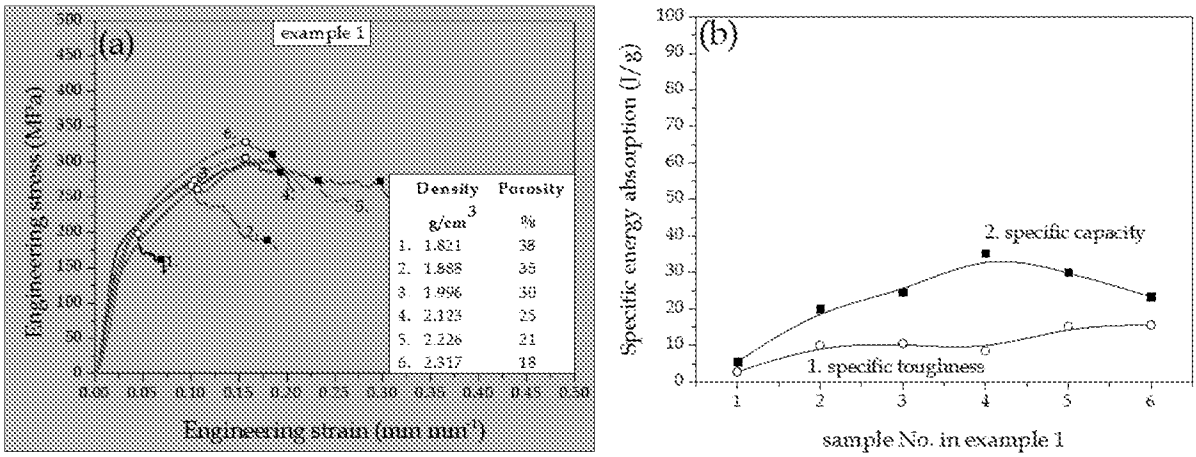

(a)
example 1
Engineering stress (MPa)
Engineering strain (mm mm-1)
Density Porosity
g/cm3 %
1. 1.821 38
2. 1.886 35
3. 1.996 30
4. 2.123 25
5. 2.226 21
6. 2.317 18
(b)
Specific energy absorption (J/g)
2. specific capacity
1. specific toughness
sample No. in example 1

FIG. 3

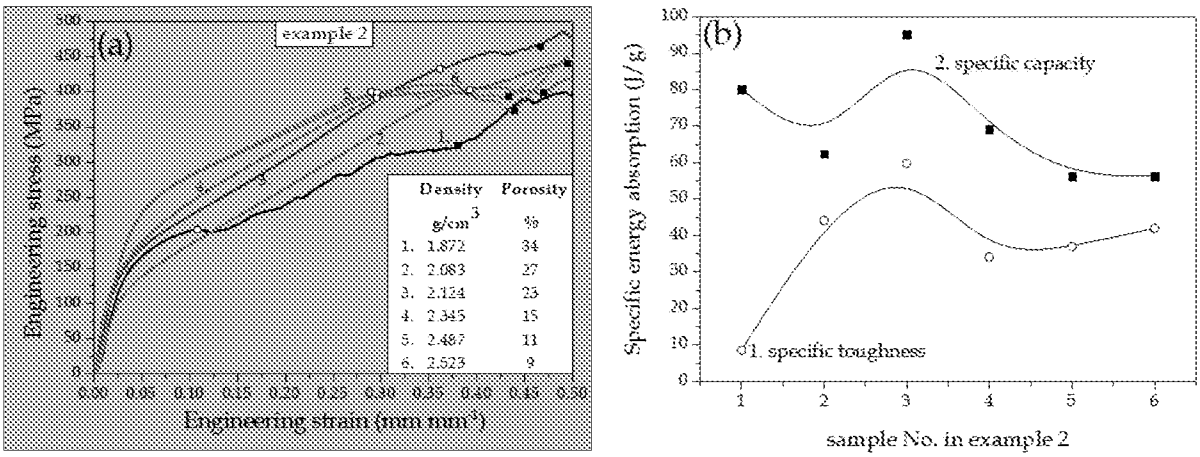

(a)
example 2
Engineering stress (MPa)
Engineering strain (mm mm-1)
Density Porosity
g/cm3 %
1. 1.872 34
2. 2.083 27
3. 2.124 23
4. 2.345 15
5. 2.487 11
6. 2.523 9
(b)
Specific energy absorption (J/g)
2. specific capacity
1. specific toughness
sample No. in example 2

FIG. 4

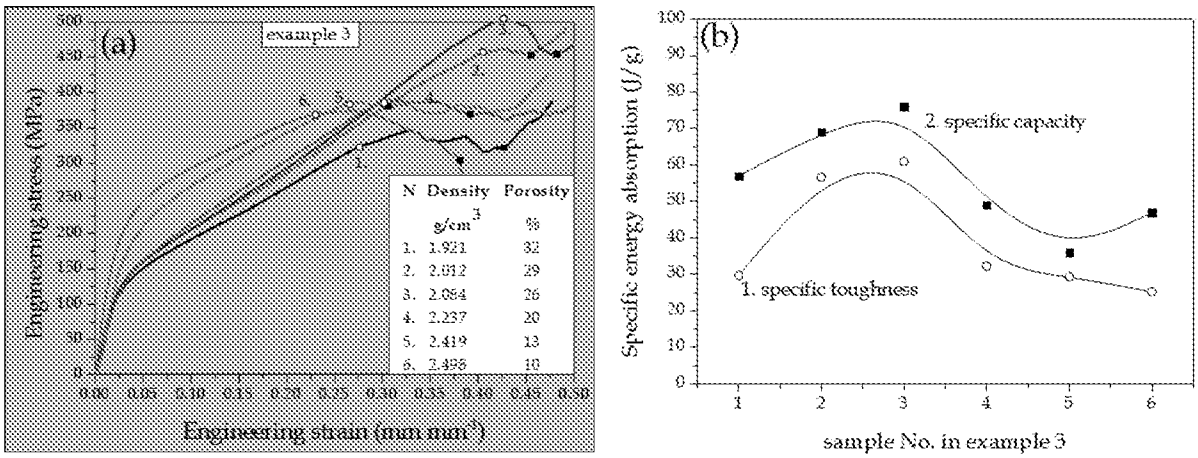

(a)
example 3
Engineering stress (MPa)
Engineering strain (mm mm-1)
N Density Porosity
g/cm3 %
1. 1.921 32
2. 2.012 29
3. 2.084 26
4. 2.237 20
5. 2.419 13
6. 2.496 10
(b)
Specific energy absorption (J/g)
2. specific capacity
1. specific toughness
sample No. in example 3

FIG. 5

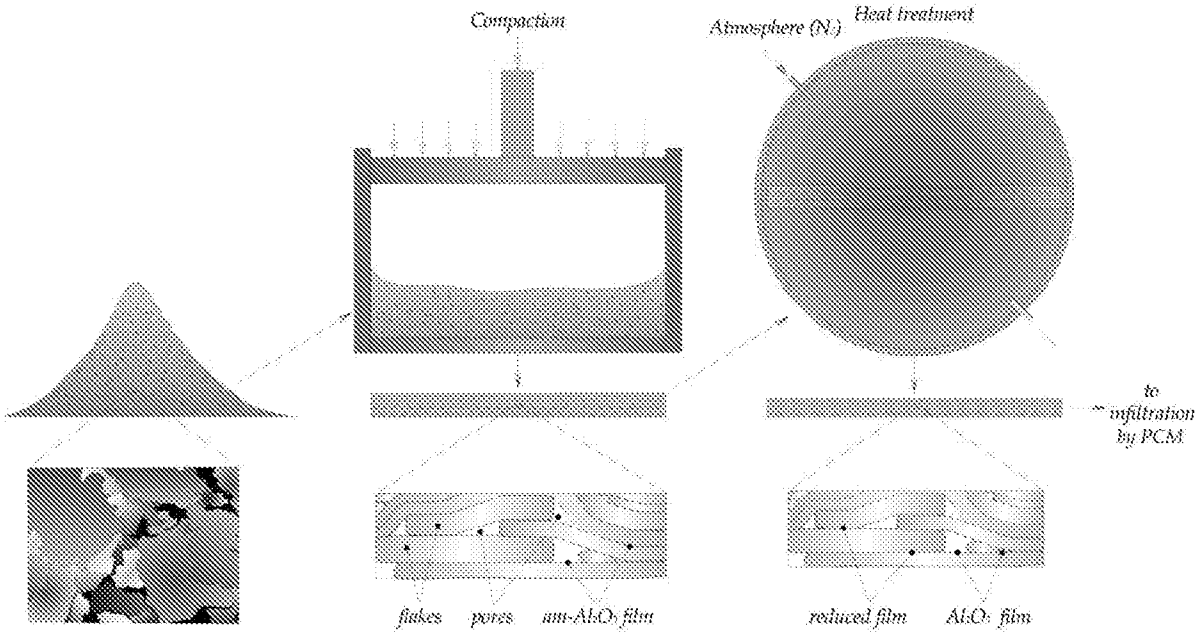

Compaction
Atmosphere (N2)
Heat treatment
to infiltration by PCM
flakes
pores
am-Al2O3 film
reduced film
Al2O3 film

FIG. 6

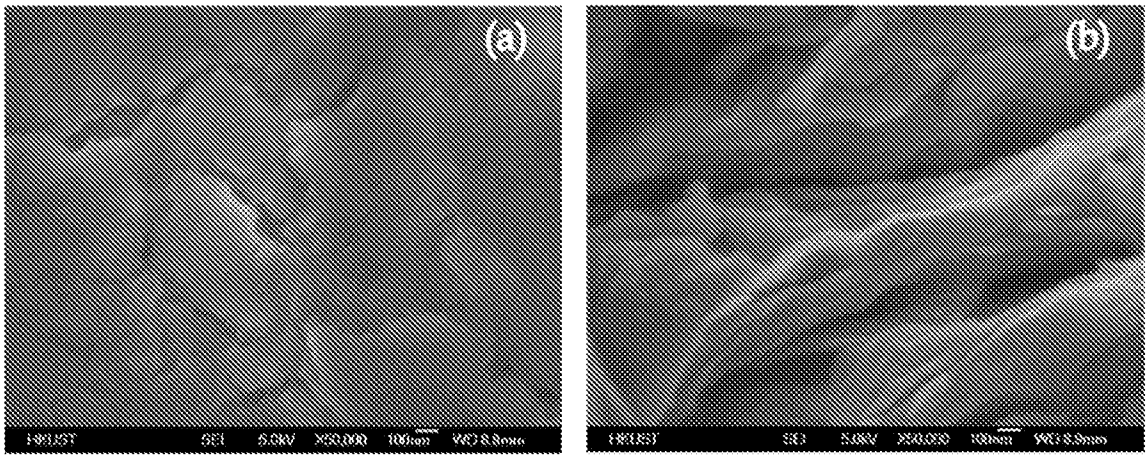

(a)
(b)

FIG. 7

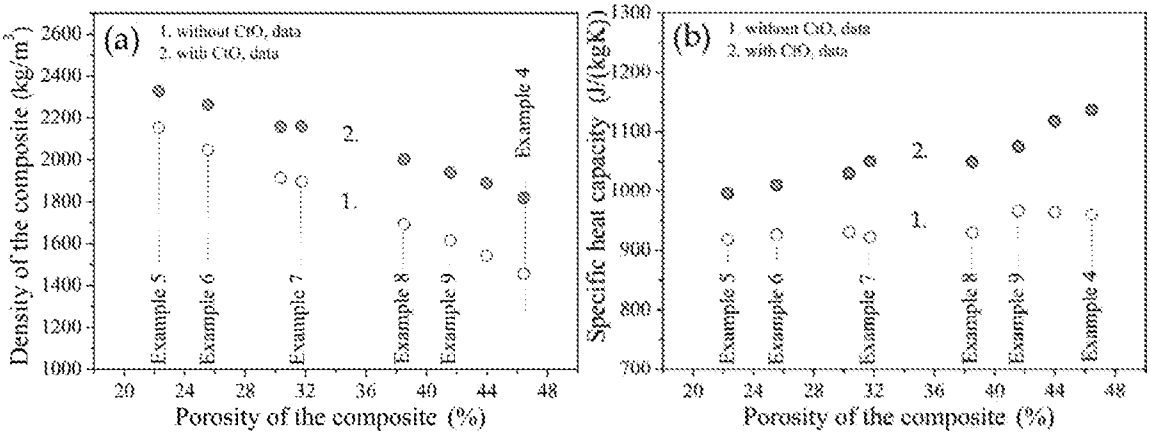

(a)
1. without CtO, data
2. with CtO, data
Density of the composite (kg/m3)
Porosity of the composite (%)
Example 5
Example 6
Example 7
Example 8
Example 9
Example 4
(b)
1. without CtO, data
2. with CtO, data
Specific heat capacity (J/(kgK))
Porosity of the composite (%)

FIG. 8

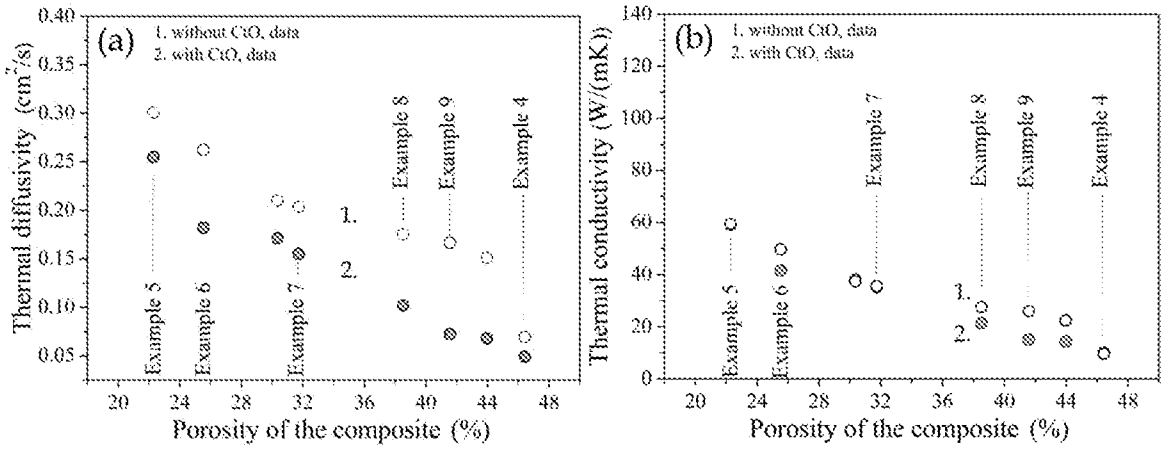

(a)
1. without CtO, data
2. with CtO, data
Thermal diffusivity (cm²/s)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
Example 5
Example 6
Example 7
Example 8
Example 9
Example 4
1.
2.
20 24 28 32 36 40 44 48
Porosity of the composite (%)
(b)
1. without CtO, data
2. with CtO, data
Thermal conductivity (W/(mK))
140
120
100
80
60
40
20
0
Example 5
Example 6
Example 7
Example 8
Example 9
Example 4
1.
2.
20 24 28 32 36 40 44 48
Porosity of the composite (%)

FIG. 9

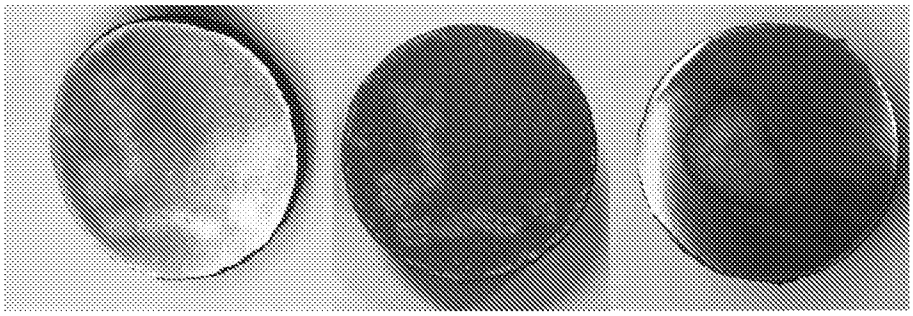

before test
tested
tested/polished

FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2017/001432

A. CLASSIFICATION OF SUBJECT MATTER

C09K 5/02(2006.01)i; C01F 7/00(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09K 5/-, C01F 7/-

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

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

CNABS, CNTXT, DWPI, SIPOABS, WEB OF SCIENCE: aluminum, porous, phase change, compact, saturated fatty acid

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 104449589 A (UNIV. BEIJING SCI. & TECHNOLOGY) 25 March 2015 (2015-03-25) description paragraphs 0006-0009	1-20
A	WO 2008054564 A1 (DOW GLOBAL TECHNOLOGIES INC. ET AL.) 08 May 2008 (2008-05-08) the whole document	1-20
A	CN 103100426 A (CHINA PETROCHEMICAL CO., LTD. ET AL.) 15 May 2013 (2013-05-15) the whole document	1-20
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A	CN 103055947 A (CHINA PETROCHEMICAL CO., LTD. ET AL.) 24 April 2013 (2013-04-24) the whole document	1-20
A	US 2011136659 A1 (ALLEN, T.L. ET AL.) 09 June 2011 (2011-06-09) the whole document	1-20

☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 February 2018	**14 March 2018**

Name and mailing address of the ISA/CN	Authorized officer
STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088** **China**	**ZHANG,Shuzhuo**
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IB2017/001432

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				CA	2723176	A1	05 November 2009
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				CN	102015095	B	08 May 2013
				US	8513154	B2	20 August 2013