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(54) **ELECTRIC CONTACT COMPRISING A METAL-GRAPHENE COMPOSITE LAYER**

(57) The invention relates to an electric contact configured to repeatedly closing and opening a conducting path by breaking and connecting an electrical circuit. The electric contact comprises a metal-graphene composite layer in which functionalized graphene is dispersed in a matrix of the metal, wherein the functionalized graphene is present in an amount within the range of from 0.05 wt% to 3 wt%.

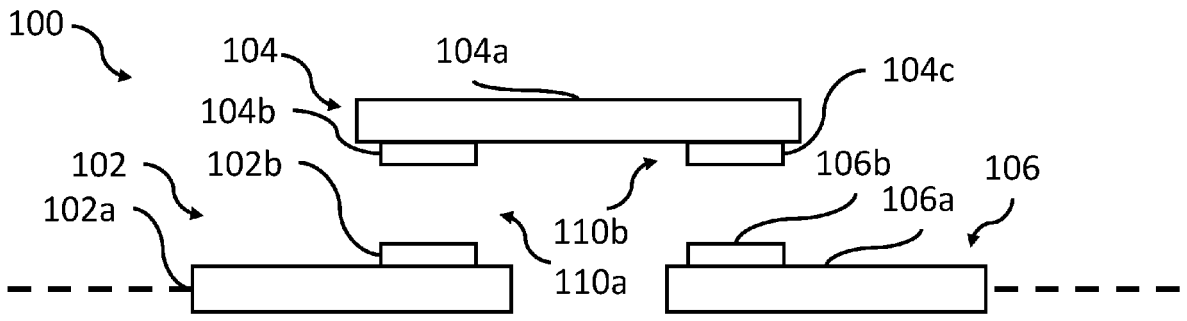

Fig. 1A

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Description

Field of the Invention

[0001] The present disclosure relates generally to an electric contact configured to repeatedly closing and opening a conducting path by breaking and connecting an electrical circuit, and in particular to a metal-graphene composite layer used the electric contact, and a method of producing the metal-graphene composite layer.

Background of the Invention

[0002] Silver (Ag)-based contact materials are commonly used in various electrical power switching devices, where low losses and stable contact performance over life are of key importance. Ag is for example used as base material in arcing contact systems in which the electric contact is configured to repeatedly close and open a conducting path by breaking and connecting an electrical circuit, owing to its electrical properties. However, the mechanical and tribological properties of Ag are not impressive. It is soft and prone to cladding onto counter surfaces. For arcing contacts this usually means high wear rate and high contact welding.

[0003] When Ag is used in an arcing contact configurations vs a copper (Cu) or Ag counter surface, a substantial amount of Ag must be added to the contact to account for wear losses. The cladding of Ag onto a counter surface creates, in essence, an Ag-Ag contact weld. There is a risk of contact welding during closing of the arcing contact (pre-arcing) and during contact bouncing. The contact welding can cause significant consequences limiting the operating time for the arcing contact. The severity of such contact welding correlates to e.g. arc energy to the contact weld strength.

[0004] Nevertheless, Ag is still used in many applications, owing to its electrical properties. For example, in low voltage applications such as low voltage switchgear, Ag is used as a matrix with an array of possible fractional additives, e.g. graphite (C), tin oxide (SnO_2) and tungsten (W). Adding for example graphite at a concentration of a few percent by weight, wt%, to the Ag matrix gives some advantageous effects. However, the hardness and density of such a composite is however limited owing to a low adhesion of the carbon surface to the Ag-matrix. This gives a high arc erosion rate for Ag-graphite components. In addition, graphene is still very expensive, which is disadvantageous from an industrial point-of-view.

[0005] There are thus several drawbacks of the current materials used for arcing contacts, and thus a need in the industry for providing an improved arcing contact and the material used therein.

Summary

[0006] An object of the present invention is to overcome at least some of the above problems, and to provide a metal-graphene composite material or layer with improved properties for an arcing contact of an electrical power switch. The invention relates to a metal-graphene composite material or layer with unusually good properties, especially as arcing. This, and other objectives, which will become apparent in the following are accomplished by means of an electric contact and a method of producing a metal-graphene composite layer.

[0007] According to a first aspect of the present invention, an electric contact configured to repeatedly closing and opening a conducting path by breaking and connecting an electrical circuit is provided. The electric contact comprises a metal-graphene composite layer in which functionalized graphene is dispersed in a matrix of the metal, wherein the functionalized graphene is present in an amount within the range of from 0.05 wt% to 3 wt%.

[0008] The functionalized graphene is typically in the form of flakes, having a thickness from a single graphene layer (Angstrom range thickness) to graphene nano-sheets (NS) having a nano-range thickness.

[0009] Functionalized graphene is here referring to graphene comprising functional groups. The functional groups are typically based on the addition of atoms or molecules other than carbon. For example, graphene oxide (GO) is considered a functionalized graphene with this definition as it comprises various oxygen containing functional groups. From a chemical point of view, the presence of oxygen functionalities at GO surface provide reactive sites for chemical modification. GO is advantageous because of its easier production and dispersion as well as simple chemical functionalization compared to graphene. For example, the presence of the oxygen functional groups at GO surface is believed to cause its hydrophilicity, on contrary to graphene which hydrophobic. Thus, an aqueous solution of GO is typically stable for a longer period of time compared to pure graphene. Moreover, without being bound by any theory, it is believed that the presence of the oxygen-containing functional groups on both sides of the GO surfaces increases the sheet thickness with respect to nonfunctionalized graphene sheets, resulting in that most of the GO sheets consist of two or three layers of graphene.

[0010] A wash process, or cleaning method, of GO that provides clean, metal- and ion-free GO flakes with uniform size distribution (small particles removed), may be used to obtain good dispersion of the GO flakes in the metal matrix. Improved dispersing of GO in the metal matrix reduces the amount of GO needed and hence limits the effect of the GO

on the electrical properties.

[0011] The use of GO, rather than non-oxidised graphene such as pure graphene, as a low-cost graphene starting material for some embodiments of the new composite contact material or layer reduces the cost. However, in other embodiments, any type of functionalized graphene, e.g. fluorinated graphene, or any mixture of functionalized graphene and graphene, may be used. Thus, according to at least one example embodiment, the functionalized graphene is graphene oxide or fluorinated graphene. According to at least one example embodiment, the term functionalized graphene is changed to "graphene oxide or fluorinated graphene". Additionally or alternatively, reduced graphene oxide, may be used.

[0012] Careful sintering of a green body of the composite, which allows gaseous species to be released from the GO flakes and escape the composite, may lead to reduction of at least some of the GO to graphene (also denoted rGO herein).

[0013] According to at least one example embodiment, the electric contact configured to repeatedly closing and opening a conducting path by breaking and connecting an electrical circuit, may be an arcing contact. The electric contact of the present invention is typically not a sliding contact, in which the contacting surface slides in relation to each other, but instead an arcing contact in which the contacting surfaces are repeatedly brought into contact with each other (closing) and brought apart (opening), the latter state indicating the contacting surfaces are not in contact with each other. According to at least one example embodiment, sliding contacts are excluded from the present invention.

[0014] The inventors have realized that by providing a metal-graphene composite layer in which functionalized graphene is dispersed in a matrix of the metal, wherein the functionalized graphene is present in an amount within the range of from 0.05 wt% to 3 wt%, an advantageous combinations of material properties, electric contact effects and low cost is achieved. For example, the metal-graphene composite layer exhibits improved anti-weld properties, with the result of reduced contact welding in the electric contact without sacrificing the good electrical properties of the pure metal. Moreover, the hardness of the material for metal-graphene composite layer is improved in relation to pure Ag, and the wear in terms of average weight loss is reduced compared to a corresponding material without the functionalized graphene. Stated differently, the electric contact of the invention exhibits low contact erosion as compared to an electric contact comprise pure Ag.

[0015] According to at least one example embodiment, the metal-graphene composite layer is a contact layer for establishing contact when closing the electric circuit.

[0016] Typically, the electric contact comprises a set of arcing contact elements or arcing contact legs, e.g. a first arcing contact element comprising the metal-graphene composite layer having a first external surface, and comprises a second contact element comprising the metal-graphene composite layer having a second external surface, which first and second external surfaces are used to be brought into contact with each other for closing the circuit, and brought apart for opening the circuit.

[0017] According to at least one example embodiment, the metal is silver, copper, gold or nickel.

[0018] Thus, instead of having Ag as the main metal of the metal-graphene composite layer, copper (Cu), gold (Au) or nickel (Ni) can be used. According to at least one example embodiment, the metal is aluminum (Al), platina (Pt), Indium (In) or tin (Sn). According to at least one example embodiment, the metal is a mixture of at least two of the following: Ag, Cu, Au, Ni, Al, Pt, In and Sn.

[0019] According to at least one example embodiment, the functionalized graphene is present in an amount within the range of from 0.05 wt% or 0.1 wt% to 0.95 wt% or 1 wt%, or within the range of from 0.05 wt% or 0.10 wt%, to 0.45 wt% or 0.5 wt%.

[0020] Thus, the advantageous effects may be achieved already at relatively low amounts, further reducing the costs. For example, by having functionalized graphene present in an amount as low as between 0.05 wt% and 0.5 wt%, both hardness of the metal-graphene composite layer, and anti-welding properties of the electric contact is sufficient.

[0021] According to at least one example embodiment, the metal-graphene composite layer is a sintered or extruded metal-graphene composite layer.

[0022] For example, sintering, in which the metal particles are diffused together to form a more solid product, similar to a cast metal product, may (e.g. for Ag) be performed at a temperature within the range of 300-500°C, e.g. at about 400°C, for a prolonged time period, e.g. at least 10 h or at least 15 h. By sintering, the density of the metal-graphene composite layer may come close to a cast metal product, e.g. metallic silver, e.g. at least 90% or at least 95% of cast metal density. Sintering may also reduce some of the GO to graphene, i.e. rGO. According to at least one example embodiment, the metal-graphene composite layer is produced by additive manufacturing, thermal spraying, cold spraying or infiltration.

[0023] According to at least one example embodiment, the metal-graphene composite layer has a hardness at 0.3 kg load of at least 70 HV, preferably at least 80 HV.

[0024] Hereby, wear of the metal-graphene composite layer in the electric contact is reduced compared to e.g. pure Ag. The hardness here is thus referring to the Vickers hardness (HV) at 0.3 kg constant load.

[0025] According to at least one example embodiment, the electric contact has a weld force below 40 N.

[0026] By such relatively low weld force, contacting welding can be reduced.

[0027] According to at least one example embodiment, the metal-graphene composite layer has a friction coefficient of 0.08-0.10.

[0028] According to at least one example embodiment, the metal-graphene composite layer comprises a metal oxide, such as e.g. tin oxide and/or zinc oxide, and/or a secondary metal, such as e.g. tungsten or chromium, and/or a carbide such as tungsten carbide.

[0029] Such additives may further improve the material properties of the metal-graphene composite layer.

[0030] According to at least one example embodiment, the functionalized graphene is homogenous distributed in the metal matrix such that the largest diameter of a metal island having no graphene oxide particles in the surface of the metal-graphene composite layer is < 2μm.

[0031] Hereby, contact welding can be reduced, as metal islands < 2μm typically do not result in arcing or pre-arcing. In other words, by such homogenous distribution of the functionalized graphene in the metal matrix, advantageous material properties of the metal-graphene composite layer can be achieved at relative low amounts of functionalized graphene.

[0032] According to at least one example embodiment, the electric contact is a low voltage switchgear or a medium voltage vacuum breaker.

[0033] Such application are particularly favorable in using the metal-graphene composite layer of the invention. For example, the operating range for the low voltage application may be between 0 and 1000 V (AC) or between 0 and 1500 V (DC). For medium voltage applications, as for the medium voltage vacuum breaker, voltages up to 38kV is possible.

[0034] According to a second aspect of the invention, a method for producing a metal-graphene composite layer for an electric contact configured to repeatedly closing and opening a conducting path by breaking and connecting an electrical circuit, is provided. The method comprising:

- suspending flakes of functionalized graphene, such as e.g. graphene oxide, in a solvent to obtain a graphene-solvent suspension, wherein the flakes have an average longest axis within the range of from 100 to 50 μm;
- suspending metal nanoparticles in a solvent to obtain a metal-solvent suspension wherein the metal is silver, copper, gold or nickel, or a combination thereof;
- mixing the metal-solvent suspension and the graphene-solvent suspension with each other; and
- evaporating the solvent from the mixture to obtain a metal-graphene composite powder having a functionalized graphene content within the range of from 0.05 wt% to 3 wt%.

[0035] Hereby, a metal-graphene composite powder wherein the functionalized graphene is well-dispersed in the matrix of the metal is provided. Such metal-graphene composite powder may be utilized when forming a metal-graphene composite layer used in the electric contact of the first aspect of the invention, with the same advantageous combinations of material properties, electric contact effects and low cost.

[0036] According to at least one example embodiment, the method comprises:

- pressing the metal-graphene composite powder to obtain a compacted composite green body.

[0037] Hereby, the density of the metal-graphene composite powder can be formed into a body having a relatively high density.

[0038] According to at least one example embodiment, the method comprises:

- sintering the composite green body at elevated temperature to obtain a sintered metal-graphene composite product, such as e.g. a metal-graphene composite layer.

[0039] Hereby, a metal-graphene composite layer having a high density may be achieved.

[0040] According to at least one example embodiment, the method comprises:

- prior to obtaining the graphene-solvent suspension, subjecting the flakes to a plurality of sequential wash cycles, wherein each of the wash cycles comprises suspension of the flakes, centrifugation of the suspension and removal of the supernatant.

[0041] Hereby, the previously mentioned wash process, or cleaning method, is provided. For example, when using GO flakes, the wash process results in clean, metal- and ion-free GO flakes with uniform size distribution (small particles removed), which may be used to obtain good dispersion of the GO flakes in the metal matrix. Improved dispersing of GO in the metal matrix reduces the amount of GO needed and hence limits the effect of the GO on the electrical properties.

[0042] According to at least one example embodiment, the solvent is ethanol. Ethanol is readily available, relatively economical, and an adequate solvent.

[0043] According to at least one example embodiment, the mixing comprises sonication.

[0044] According to at least one example embodiment, the flakes are graphene oxide nano sheets.

[0045] It is to be noted that any feature of any of the aspects may be applied to any other aspect, wherever appropriate. Likewise, any advantage of any of the aspects may apply to any of the other aspects. Other objectives, features and advantages of the enclosed embodiments will be apparent from the following detailed disclosure, from the attached dependent claims as well as from the drawings.

[0046] Generally, all terms used in the claims are to be interpreted according to their ordinary meaning in the technical field, unless explicitly defined otherwise herein. All references to "a/an/the element, apparatus, component, means, step, etc." are to be interpreted openly as referring to at least one instance of the element, apparatus, component, means, step, etc., unless explicitly stated otherwise. The steps of any method disclosed herein do not have to be performed in the exact order disclosed, unless explicitly stated. The use of "first", "second" etc. for different features/components of the present disclosure are only intended to distinguish the features/components from other similar features/components and not to impart any order or hierarchy to the features/components.

Brief Description of the Drawings

[0047] These and other aspects of the present inventive concept will now be described in more detail, with reference to the appended drawings showing an example embodiment of the inventive concept, wherein:

Fig. 1A - 1B conceptually illustrates an arcing contact arrangement for an electrical switching device in accordance with an example embodiment of the invention;

Fig. 2 illustrates an example of mixing suspended Ag nanoparticles (NP) with suspended GO flakes to obtain a metal-composite powder in accordance with an example embodiment of the invention.

Fig. 3 is a graph showing the weld force vs arc energy of different metal-graphene composite layers compared with a pure Ag reference sample;

Fig. 4 is a graph showing the wear rate between a metal-graphene composite layer and a pure Ag reference sample;

Fig. 5 is a flowchart of a method of producing a metal-graphene composite layer in accordance with example embodiments of the invention.

Detailed Description of Example Embodiments

[0048] In the present detailed description, various embodiments of the present invention are herein described with reference to specific implementations. In describing embodiments, specific terminology is employed for the sake of clarity. However, the invention is not intended to be limited to the specific terminology so selected. While specific exemplary embodiments are discussed, it should be understood that this is done for illustration purposes only. A person skilled in the relevant art will recognize that other components and configurations can be used without parting from the scope of the invention.

[0049] Figs. 1A and 1B conceptually illustrates an arcing contact arrangement 100 (which may simply be referred to as an arcing contact) for an electrical switching device such as low voltage switchgears, low voltage contactors, low voltage circuit breakers, low voltage switch disconnectors, manual motor starters, although other devices are also conceivable, e.g. medium voltage vacuum breakers.

[0050] The arcing contact arrangement 100 comprises a set of arcing contact elements or arcing contact legs, a first arcing contact element 102, a second arcing contact element 104, and a third arcing contact element 106. Each of the arcing contact elements 102, 104, 106 comprises a substrate 102a, 104a, 106a. A first substrate 102a comprises a metal-graphene composite layer 102b forming an electric contact, a second substrate 104a comprises two metal-graphene composite layer 104b, 104c, forming a respective electric contact, and a third substrate 106a comprises a metal-graphene composite layer 106b forming an electric contact.

[0051] The metal-graphene composite layer, used as metal-graphene composite layers 102b, 104b, 104c, 106b in Figs. 1A-1B, is a layer in which functionalized graphene is dispersed in a matrix of the metal, wherein the functionalized graphene is present in an amount within the range of from 0.05 wt% to 3 wt%. The metal, and corresponding matrix of metal, is preferably Ag. Although Ag is preferred and used as an example of the base metal of the metal-graphene composite layer discussed herein, any other suitable electrically conducting metal, or combination thereof, such as Cu, Au or Ni, may be used instead. The functionalized graphene is preferably graphene oxide. However, the functionalized graphene may be functionalized with another substance, e.g. flour, F, and thus be fluorinated graphene.

[0052] The substrates 102a, 104a, 106a and the corresponding metal-graphene composite layers 102b, 104b, 104c, 106b are arranged such that two arcing contacts 110a, 110b are formed, a first arcing contact 110a between the metal-graphene composite layer 102b of the first arcing contact element 102 and a first metal-graphene composite layer 104b of the second arcing contact element 104, and a second arcing contact 110b between the metal-graphene composite

layer 106b of the third arcing contact element 106 and a second metal-graphene composite layer 104c of the second arcing contact element 104. By bringing the arcing contacts 110a, 110b into an open state and a closed state, electricity is able to flow from the first arcing contact element 102 to the third arcing contact element 106, via the third arcing contact element 104 (open state of the contact) and prevented to flow from the first arcing contact element 102 to the third arcing contact element 106, via the third arcing contact element 104 (closed state of the contact), respectively.

[0053] Fig. 1A illustrates the conceptual arcing contact arrangement 100 in the open state in which no electrical current flows through the arcing contact 100. In other words, the metal-graphene composite layers 102b, 104b of the first and second arcing contact elements 102, 104 in the first arcing contact 110a, as well as the metal-graphene composite layers 106b, 104c of the third and second arcing contact elements 106, 104, in the second arcing contact 110b are brought apart. In a closed state, shown in Fig. 1b, the external surfaces of the metal-graphene composite layers 102b, 104b of the first and second arcing contact elements 102, 104 in the first arcing contact 110a, as well as the external surfaces of the metal-graphene composite layers 106b, 104c of the third and second arcing contact elements 106, 104, in the second arcing contact 110b are brought into contact with each other, whereby an electrical current / may flow from a current inlet at the first arcing contact element 102 and via the first arcing contact 110a to the second arcing contact 110b, subsequently to the third arcing contact element 106. Thus, the metal-graphene composite layers 102b, 104b, 104c, 106b are contact layers for establishing contact when closing the electric circuit. The second arcing contact element 104 may be e.g. spring loaded in order to maintain the arcing contact arrangement in the closed state as shown in Fig. 1B.

[0054] When transitioning between open and closed states of an arcing contact arrangement similar to that of Fig. 1, but in which the metal-graphene composite layers 102b, 104b, 104c, 106b are exchanged with e.g. pure metal layers (e.g. pure Ag or Cu), arcs between the contacting arcing elements 102, 104, 106, may occur, as well as contact welding between first and second arcing contacts 110a, 110b. By using metal-graphene composite layers 102b, 104b, 104c, 106b of the invention, such problems are reduced without sacrificing the good electrical properties of the pure metal. It should be noted that not both electrical contacts in each of the arcing contacts 110a, 110b need to comprise such metal-graphene composite layer. For example, the first substrate 102a may comprise an electric contact different to the metal-graphene composite layer, while the second substrate 104a and its first electric contact 104b is formed by the metal-graphene composite layer.

[0055] Thus, the arcing contact 100 is configured to repeatedly closing and opening a conducting path (i.e. by means of the first arcing contact 110a, and/or the second arcing contact 110b) by breaking and connecting an electrical circuit (i.e. a circuit from the first arcing contact element 102 to the third arcing contact element 106). The operation of an arcing contact arrangement is assumed to be known per se to the skilled person and will not be described in more detail.

[0056] An example method for producing such metal-graphene composite layer will now be described with reference to Fig. 2. Fig. 2 illustrates embodiments of a method of producing the metal-graphene composite powder, used for the metal-graphene composite layer. In these embodiments, the metal is Ag, and Ag particles 1 or Ag nanoparticles, AG NP, 1 are suspended in a solvent 3 to form a metal suspension 5. The solvent 3 may be any suitable solvent, e.g. water or ethanol, or a mixture thereof, preferably polar and environmentally friendly solvent options. In parallel, the graphene in the form of functionalized graphene, here graphene oxide, GO, flakes, 2 e.g. graphene oxide nano flakes, GO NS, 2 are suspended in a solvent 3, e.g. the same or similar solvent as in the metal suspension, to form a graphene suspension 7. It should be noted that in addition to the GO NS, graphene flakes, e.g. graphene NS may be present in solvent 3. The GO flakes, or graphene flakes, preferably have an average longest axis as measured within the range of from 100 nm to 50 μm, 30 μm, 10 μm 1 μm or 500 nm, e.g. within a range of from 1 or 10 to 20 μm, and an average thickness of at most ten graphene layers. The graphene suspension 7 may be sonicated to prevent agglomeration of the flakes in the suspension. When flakes, e.g. NS, are discussed herein, it is understood that at least some of the GO or graphene in the flakes may be in the form of reduced graphene oxide, rGO.

[0057] The metal suspension 5 and the graphene suspension 7 are mixed, e.g. by adding the graphene suspension 7 to the metal suspension 5, to form a mixture to form a metal-graphene mixture 9 or metal-graphene suspension 9. In some embodiments, the metal-graphene mixture 9 is sonicated to further improve the mixing and dispersion of the GO flakes 2 with the Ag particles 1 and to prevent agglomeration of the flakes in the suspension. There is preferably no chemical reaction taking place between the Ag particles 1 and GO flakes 2 during the mixing. The mixing is for obtaining good dispersion of the GO flakes 2. Such dispersion results in that the GO is homogenous distributed in the metal matrix. Hereby, in the final product, i.e. the metal-graphene composite layer, the largest diameter of a metal island having no graphene oxide particles in the surface may be < 2μm.

[0058] The GO flakes 2 are preferably present in an amount of less than 1, 0.95, 0.5, 0.45, 0.2 or 0.1 wt% of the combination of the GO flakes 2 and the Ag particles 1 in the suspension, such as within the range of from 0.05 wt% to 0.5, or 0.45 wt%. For instance, a suspension of 0,005 g GO flakes 2 (e.g. in 100 mL ethanol) may be mixed into a suspension of 10 g Ag particles NP (e.g. in 500 mL ethanol). Drop mixing may be preferred in order to make sure that the GO flakes 2 are properly dispersed in the mixture, avoiding agglomeration. For instance, the graphene suspension 5 may be drop mixed into the metal suspension 3 during at least 20 or 30 minutes to obtain a metal-graphene suspension

9 having a dry weight of about 10 g.

[0059] Then, the solvent is evaporated from the metal-graphene suspension 9 to form a metal-graphene composite powder, e.g. an Ag-GO composite powder in this case. To reduce the energy needed for the evaporation, a relatively volatile solvent may be preferred, e.g. ethanol, which may be recycled to save cost and the environment. The evaporation of the solvent may be followed by drying of the metal-graphene composite powder at an elevated temperature of e.g. at least 80°C such as at about 100°C to remove traces of solvent and/or water.

[0060] In order to improve the quality of the graphene suspension 7 and final composite product, with relatively pure graphene having a relatively uniform flake size distribution and low amount of agglomeration, the GO flakes 2 are preferably washed and centrifuged before mixing with the Ag particles 1. In some embodiments, prior to obtaining the graphene suspension 7, the GO flakes 2 are subjected to a plurality of sequential wash cycles, wherein each of the wash cycles comprises suspension of the GO flakes 2, centrifugation of the suspension and removal of the supernatant.

[0061] Thus, an objective of the wash process is to purify GO The process reduces the amount of inorganic impurities, increases the pH of aqueous purified GO solutions towards neutral, and decrease the proportion of small, highly oxidized carbonaceous components. The new process may involve ultra-sonication and (ultra-)centrifugation-assisted sedimentation. The process is efficient, limits aggregation of the purified GO flakes and allows a change of solvent for the GO solution/suspension/paste from water to water-miscible organic solvents such as low-boiling alcohols, e.g. ethanol.

[0062] In example embodiments of the wash process, the suspension of GO in water (e.g. 3-4 mg impure GO/mL) may be mixed with the same volume of ethanol (e.g. 99% pure) with bath sonication for at least 10 minutes, after which the mixture is transferred to appropriate centrifugation flasks. Centrifugation at medium speed (5000-6000 g) for 4-8 hours sediments the GO, leaving the most soluble impurities in the supernatant. Removal of the supernatant, without disturbing the sediment material, leaves a concentrated water-ethanol suspension of GO of higher purity. Fresh ethanol is added, followed by sonication, centrifugation and supernatant removal, this sequence may be repeated 2-4 times with centrifugation speed increasing and centrifugation time decreasing for each wash cycle. When GO has reached sufficient purity and the water content is low enough, the supernatant is colourless and the sedimented GO, after removal of the supernatant, has a gel-like appearance and a GO concentration of 30-40 mg/mL. This concentrated GO gel may be dissolved/suspended in water and in water-miscible organic solvents.

[0063] Well-dispersed GO flakes in an Ag matrix enhances tribological properties and performance without sacrificing the electrical properties of pure Ag. By the wash process, that efficiently removes metallic and ionic residues and narrows flake size distribution, as well as a wet mixing protocol, a well dispersed Ag-GO nanocomposite product may be obtained. This improves the anti-welding properties of the material. It has also been shown that with well-dispersed GO flakes, very small amounts of GO (e.g. 0.01 wt%) is enough to dramatically reduce the friction coefficient compared with using pure Ag in dry conditions (from about 1.4-1.5 for pure Ag to about 0.08-0.09 for the Ag-GO (0.01 wt%) composite layer) and increase wear resistance without sacrificing the electrical properties of Ag.

[0064] An objective of the wash process is to separate GO into, preferably, monolayer sheets and disperse them as evenly possible in a metal matrix. The method includes a wet mixing process, suspending both metal nanoparticles, as Ag NP 1, and cleaned GO flakes 2 as discussed in relation to Fig. 2, first separately in ethanol suspensions and then mixing together the two suspensions and evaporating the solvent 3 to get a well-dispersed e.g. Ag-GO mixture. This mixture may then be pressed and sintered into the final contact material and the metal-graphene composite layer.

[0065] For example, the obtained metal-graphene composite powder may be compacted to a green body e.g. at room temperature and a pressure of at least 400 MPa or 500 MPa, e.g. within the range of 400-600 MPa, which may be preferred for Ag NP 1. By compacting, the density of the metal-graphene composite product may come closer to a cast metal product, e.g. metallic silver, e.g. at least 70% or at least 80% or at least 85% of cast metal density.

[0066] The green body may be used for the arcing contact, or the green body may be sintered, and the sintered product be used for the arcing contact.

[0067] Sintering, in which the metal particles are diffused together to form a more solid product, similar to a cast metal product, may (e.g. for silver) be performed at a temperature within the range of 300-500°C, e.g. at about 400°C, for a prolonged time period, e.g. at least 10 h or at least 15 h. By sintering, the density of the metal-graphene composite layer may come close to a cast metal layer, e.g. metallic silver, e.g. at least 90% or at least 95% of cast metal density. Sintering may also reduce some of the GO to graphene, i.e. rGO. Thus, the metal-graphene composite layer may be a sintered metal-graphene composite layer.

[0068] By using the metal-graphene composite material or metal-graphene composite layer in at least one of the electric contacts in an arcing contact (i.e. at least one of the contacts in a contact pair) of an electric power application, an advantageous combinations of material properties, electric contact effects and low cost is achieved. For example, the metal-graphene composite layer exhibits improved anti-weld properties, with the result of reduced contact welding in the electric contact without sacrificing the good electrical properties of the pure metal since the amount of GO dispersed in the metal matrix can be kept low thanks to embodiments of the method of producing the metal-graphene composite layer of the present invention. Moreover, the hardness of the material for metal-graphene composite layer is improved in relation to pure Ag, and the wear in terms of average weight loss is reduced compared to a corresponding material

without the functionalized graphene. This advantageous effects of the metal-graphene composite layer is exemplified in the below examples.

Examples

[0069] With reference to Fig. 3, the weld force vs arc energy were measured for pure Ag layers and metal-graphene composite layers in the form of Ag-GO composite layer by an electric circuit using a mechanical switch, somewhat simplified compared to the arcing contact arrangement 100 of Fig. 1. For Fig. 3, an arcing contact arrangement comprising a first and second arcing contact element, each comprising a circular copper rod with a corresponding contact tip/layer comprising the material to be compared (i.e. Ag, and Ag-GO composites) was used. The first and second arcing contact elements were brought together for closing the arcing contact arrangement (to form an Ag/Ag interface, or Ag-GO/Ag-GO interface), the closing being performed during an arc, and were subsequently brought apart when opening the arcing contact arrangement. In a closed state of the mechanical switch, an electric pulse was allowed to flow through the circuit, where after a tensiometer was used to measure the force needed to bring the mechanical switch into an open state. Two different Ag-GO composite layers (sintered green bodies) were formed, one with 0.5 wt % GO and one with 3 wt% GO, represented as Ag-GO 0.5wt% and Ag-GO 3wt%, respectively.

[0070] The pure Ag reference show significantly higher weld forces for corresponding arc energies compared to the two Ag-GO composite layers. Thus, when adding GO in different amount to the Ag matrix, the weld force drops significantly compared with the pure Ag reference. At a concentration of only 0.05 wt%, the weld force is always below 30 N and in a majority of the measurements, below 20 N, while for the Ag reference, almost all registered measurements are above 30 N, often as high as about 60 - 120 N.

[0071] Moreover, the Vickers hardness at 0.3 kg were measured for pure Ag layers and metal-graphene composite layers in the form of Ag-GO composite layer by a Vickers hardness measurement at 0.3 kg load (i.e. a Vickers-impression is made with a diamond in the form of a square-based pyramid at the specified load of 0.3 kg, where after the area of the impression is measured and compared with the load. Two different Ag-GO composite layers (sintered green bodies) were formed, one with 0.05 wt % GO and Ag nano particles, and one with 0.05 wt% GO with Ag micro particles, and two different Ag layers, one with a density of 100 % and one with density of 96.3 % (the density here being related to the theoretical density of the respective material in the layers, and is thus a measure of the effectiveness of the sintering process).

[0072] As shown in Table 1, the hardness of the two Ag-GO composite layers are significantly higher than the pure Ag references.

Sample ID	Material	Density %	Hardness, HV
1	Ag-GO 0.05 wt% nano particles	93.0	81
2	Ag-GO 0.05 wt% micro particles	92,9	74
3	Ag reference	100	66
4	Ag reference	96,3	67

[0073] Thus, when adding GO to the Ag matrix, the hardness increases significantly compared with the pure Ag reference. At a concentration of only 0.05 wt%, the hardness is above 70 HV, even when Ag micro particle are used, and as high as 80 HV when Ag nano particles are used.

[0074] With reference to Fig. 4, tribological pin-on-disc measurements were carried out on pure Ag, and an Ag-GO composite layers with 0.01 wt% GO, respectively, at a constant contact load of 5 N and with a counter contact being an Ag-coated Cu pin. The wear of a pure Ag contact is difficult to measure as the Ag is soft and tend to clad and re-clad back and forth between the two interacting external (contacting) surfaces. Ploughing also occurs. An uneven wear track is formed, due to the cladding behavior. On the other hand, the Ag-GO composite layer with 0.01 wt% GO arranged on corresponding interacting external (contacting) surfaces and exposed to 10 000 operations (i.e. brought into contact and brought apart) showed a much smoother and less worn wear track. Comparing the wear rates of these two samples (wear volume normalized to the load and wear length), the Ag-GO composite layer had a significantly lower wear rate than the pure Ag reference, as shown in Fig. 4.

[0075] Contact resistance measurements carried out using an Ag-coated Cu probe, under different contact loads, showed very similar data for pure Ag compared to an Ag-GO composite layer with 0.01 wt% GO. This indicates a very minor contribution from the GO component in the composite material, which essentially behaves electrically like pure Ag.

[0076] The Ag-GO composite layer with 0.01 wt% GO, as analyzed by light-optical microscopy (LOM), revealed an even distribution of large graphene oxide sheets in the Ag matrix.

[0077] Scanning electron microscopy (SEM) showed thin, transparent GO sheets with dispersed Ag nanoparticles above and below the sheets. This suggests well-separated GO and Ag particles. The transparency of the GO sheets indicates that they contain mono-layers or few layers of GO stacked on top of each other.

[0078] When regular dry-powder mixing is used instead of the wet mixing process of the present disclosure, GO flakes have a strong tendency to stick together. Also, when contaminated GO is used, the composite will not be well-dispersed and the GO flakes agglomerate into GO lumps.

[0079] Fig. 5 is a flow-chart comprising the steps of a method for producing a metal-graphene composite layer for an electric contact configured to repeatedly closing and opening a conducting path by breaking and connecting an electrical circuit. The method is partly overlapping with the method described with reference to Fig. 2.

[0080] In a step S1, flakes of functionalized graphene, such as e.g. graphene oxide, are suspended in a solvent to obtain a graphene-solvent suspension. The flakes typically has an average longest axis within the range of from 100 to 50 μm.

[0081] In a step S3, metal nanoparticles, such as Ag nanoparticles, are suspended in a solvent to obtain a metal-solvent suspension.

[0082] In a step S5, the metal-solvent suspension and the graphene-solvent suspension are mixed with each other, forming a mixture.

[0083] In a step S7, the solvent is evaporated from the mixture to obtain a metal-graphene composite powder having a functionalized graphene content within the range of from 0.05 wt% to 3 wt%.

[0084] Thus, steps S1, S3, S5 and S7 are corresponding to the method described with reference to Fig. 2.

[0085] Moreover, the method may comprise the following steps:
In a step S9, the metal-graphene composite powder is pressed to obtain a compacted composite green body.

[0086] In a step S11, the composite green body is sintered at elevated temperature to obtain a sintered metal-graphene composite product, such as e.g. a metal-graphene composite layer.

[0087] In a step S0, occurring prior to the step S1, the flakes are subjected to a plurality of sequential wash cycles, wherein each of the wash cycles comprises suspension of the flakes, centrifugation of the suspension and removal of the supernatant.

[0088] The present disclosure has mainly been described above with reference to a few embodiments. However, as is readily appreciated by a person skilled in the art, other embodiments than the ones disclosed above are equally possible within the scope of the present disclosure, as defined by the appended claims.

Claims

1. An electric contact configured to repeatedly closing and opening a conducting path by breaking and connecting an electrical circuit, the electric contact comprising a metal-graphene composite layer in which functionalized graphene is dispersed in a matrix of the metal, wherein the functionalized graphene is present in an amount within the range of from 0.05 wt% to 3 wt%.

2. The electric contact according to claim 1, wherein the metal is silver, copper, gold or nickel.

3. The electric contact according to any one of the preceding claims, wherein the functionalized graphene is graphene oxide or fluorinated graphene.

4. The electric contact according to any one of the preceding claims, wherein the functionalized graphene is present in an amount within the range of from 0.05 wt% or 0.1 wt% to 0.95 wt% or 1 wt%, or within the range of from 0.05 wt% or 0.10 wt%, to 0.45 wt% or 0.5 wt%.

5. The electric contact according to any one of the preceding claims, wherein the metal-graphene composite layer is a sintered or extruded metal-graphene composite layer.

6. The electric contact according to any one of the preceding claims, wherein the metal-graphene composite layer has a hardness with 10 g load of at least 90 HV and/or a hardness with a 50 g load of at least 75 HV.

7. The electric contact according to any one of the preceding claims, wherein the metal-graphene composite layer is a contact layer for establishing contact when closing the electric circuit.

8. The electric contact according to any one of the preceding claims, wherein the metal-graphene composite layer comprises a metal oxide, such as e.g. tin oxide and/or zinc oxide, and/or a secondary metal, such as e.g. tungsten

or chromium, and/or a carbide such as tungsten carbide.

9. The electric contact according to any one of the preceding claims, wherein the functionalized graphene is homogenous distributed in the metal matrix such that the largest diameter of a metal island having no graphene oxide particles in the surface of the metal-graphene composite layer is < 2μm.

10. The electric contact according to any one of the preceding claims, being a low voltage switchgear or a medium voltage vacuum breaker.

11. A method of producing a metal-graphene composite layer for an electric contact configured to repeatedly closing and opening a conducting path by breaking and connecting an electrical circuit, the method comprising:

- suspending flakes of functionalized graphene, such as e.g. graphene oxide, in a solvent to obtain a graphene-solvent suspension, wherein the flakes have an average longest axis within the range of from 100 to 50 μm;
- suspending metal nanoparticles in a solvent to obtain a metal-solvent suspension wherein the metal is silver, copper, gold or nickel, or a combination thereof;
- mixing the metal-solvent suspension and the graphene-solvent suspension with each other; and
- evaporating the solvent from the mixture to obtain a metal-graphene composite powder having a functionalized graphene content within the range of from 0.05 wt% to 3 wt%.

12. The method according to claim 11, comprising:

- pressing the metal-graphene composite powder to obtain a compacted composite green body.

13. The method according to claims 12, comprising:

- sintering the composite green body at elevated temperature to obtain a sintered metal-graphene composite product, such as e.g. a metal-graphene composite layer.

14. The method according to any one of claims 11-13, comprising:

- prior to obtaining the graphene-solvent suspension, subjecting the flakes to a plurality of sequential wash cycles, wherein each of the wash cycles comprises suspension of the flakes, centrifugation of the suspension and removal of the supernatant.

15. The method according to any one of claims 11-14, wherein the flakes are graphene oxide nano sheets.

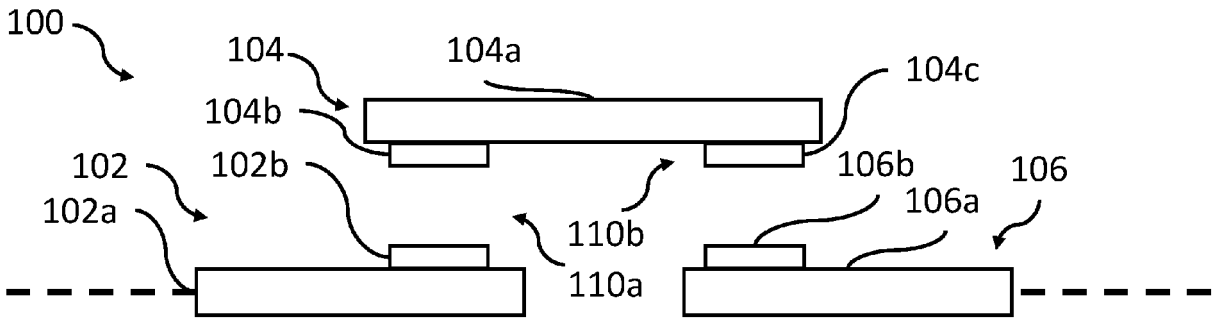
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Fig. 1A

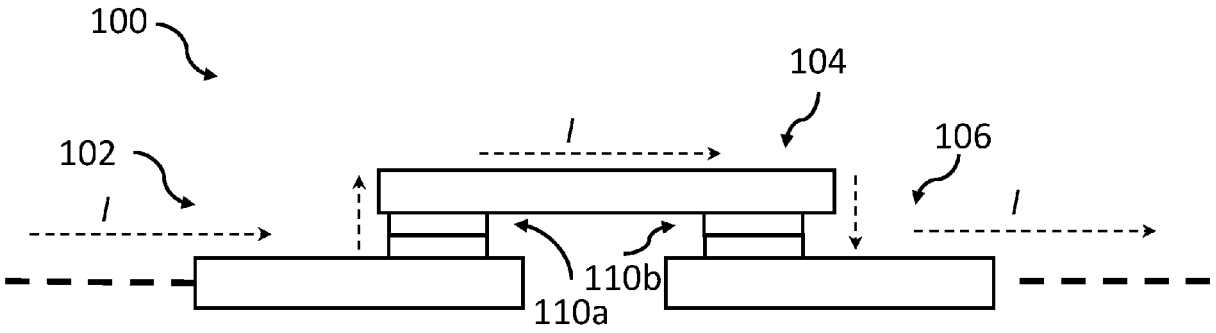
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Fig. 1B

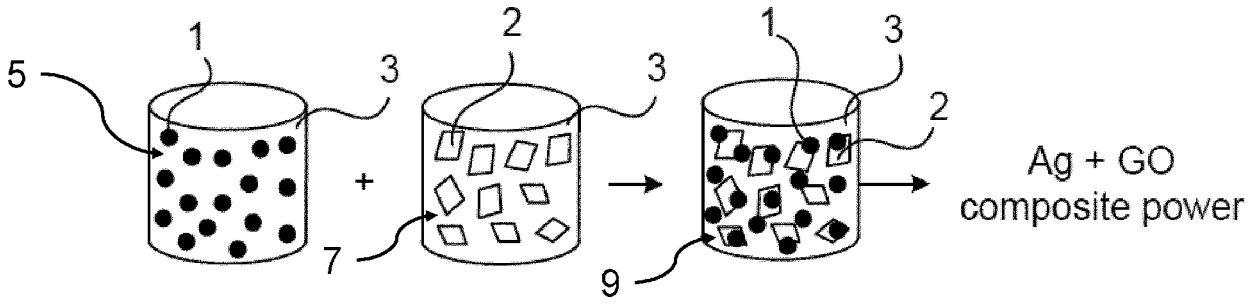

Fig. 2

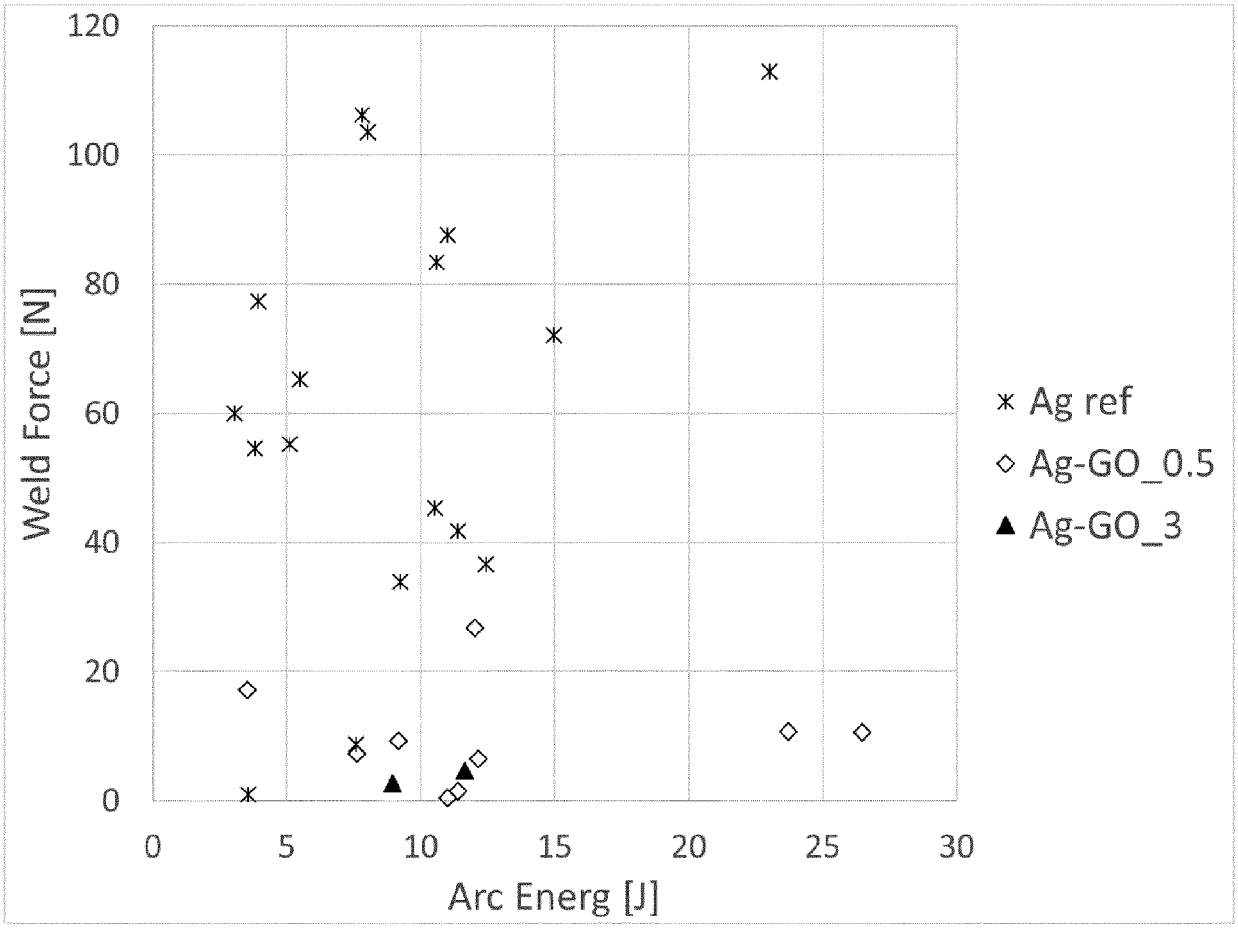
120
100
80
60
40
20
0
Weld Force [N]
0
5
10
15
20
25
30
Arc Energ [J]
Ag ref
Ag-GO_0.5
Ag-GO_3

Fig. 3

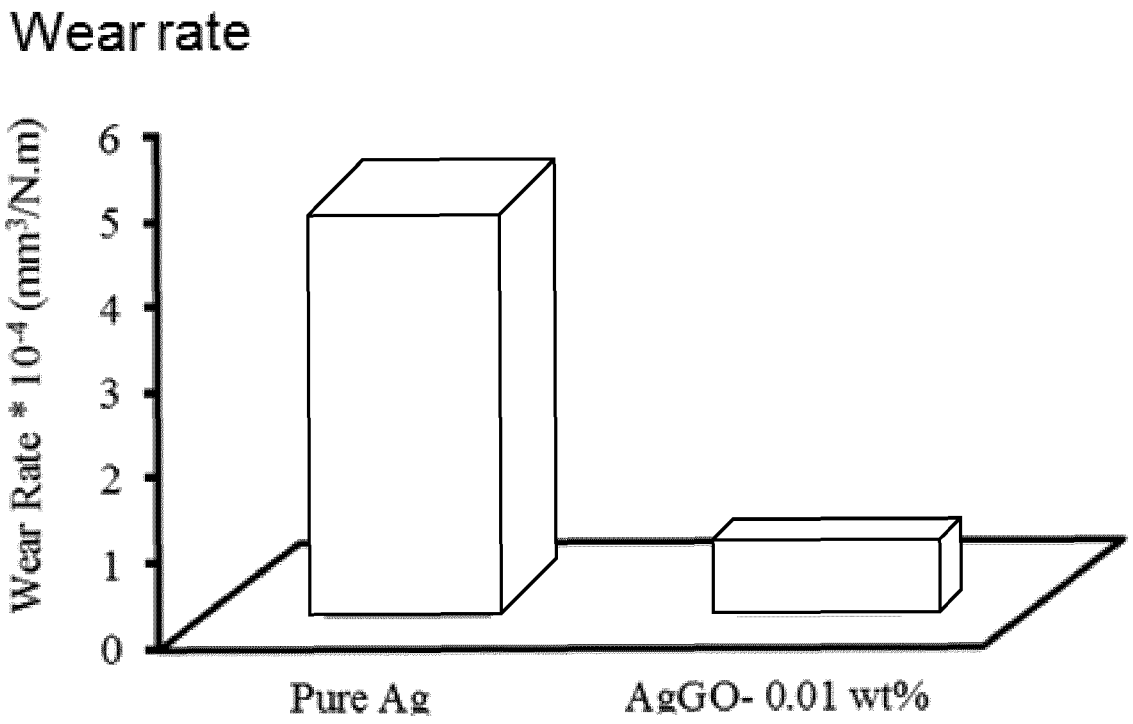

Fig. 4

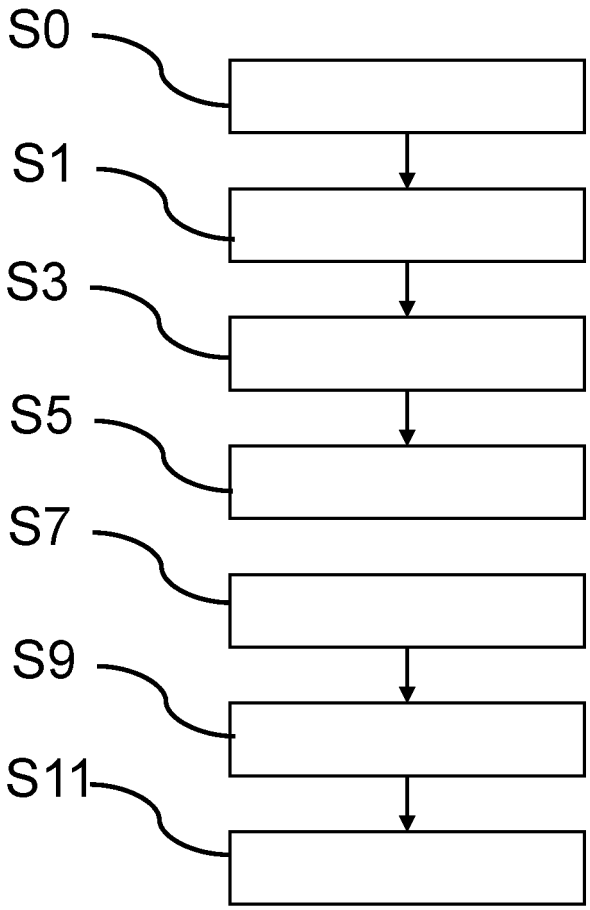

Fig. 5

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EUROPEAN SEARCH REPORT

Application Number
EP 20 19 7503

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 2018/189146 A1 (ABB SCHWEIZ AG [CH]) 18 October 2018 (2018-10-18) * page 1, lines 3,4 * * page 2, line 29 - page 3, line 12 * * page 3, lines 7-20 * * page 4, lines 5,6, 23-25 * * page 6, lines 3-6,17-29 * * page 7, lines 3-5, 21-23 * * page 7, line 29 - page 8, line 30 * * page 9, lines 4-23 * * claim 5 *	1-5,7,9, 11-15	INV. H01H1/021 H01H1/0237 H01H1/027 H01H11/04 B22F1/00
X	CN 110 484 803 A (UNIV HENAN SCIENCE & TECH) 22 November 2019 (2019-11-22) * paragraphs [0002], [0072]; claims 1,2 *	1-8,10	
			TECHNICAL FIELDS SEARCHED (IPC) H01H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	3 March 2021	Ramírez Fueyo, M

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03-03-2021

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2018189146 A1	18-10-2018	CN 110573272 A	13-12-2019
		EP 3388168 A1	17-10-2018
		KR 20190119157 A	21-10-2019
		US 2020152399 A1	14-05-2020
		WO 2018189146 A1	18-10-2018
CN 110484803 A	22-11-2019	NONE	

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