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(54) Title: METHOD FOR FORMING AN ELECTRICALLY CONDUCTIVE MULTILAYER COATING WITH ANTI-CORROSION PROPERTIES ONTO A METALLIC SUBSTRATE

(57) Abstract: The invention is directed to a method for forming an electrically conductive multilayer coating with anti-corrosion properties and with a thickness comprised between 1 μm and 10 μm onto a substrate, comprising the following subsequent steps of (a) providing a suspension consisting of electrically conductive fillers into a matrix forming material; (b) depositing said suspension on at least a surface portion of a substrate; (c) exposing an atmospheric pressure plasma to said surface portion so as to form one electrically conductive layer with anti-corrosion properties; and (d) repeating said steps (a), (b) and (c). Said method is remarkable in that said electrically conductive fillers are electrically conductive particles.
METHOD FOR FORMING AN ELECTRICALLY CONDUCTIVE MULTILAYER COATING WITH ANTI-CORROSION PROPERTIES ONTO A METALLIC SUBSTRATE

Description

Technical field

[0001] The present invention is directed to the field of electrically conductive and corrosion-resistant composite coatings. In particular, the invention relates to a method for forming electrically conductive and corrosion-resistant composite multilayer coating using atmospheric-pressure plasma discharges.

Background art

[0002] Fanelli F. et al., (study entitled "Aerosol-assisted atmospheric cold plasma deposition and characterization of superhydrophobic organic-inorganic nanocomposite thin films", in Langmuir, 2014, 30, 857-865) have demonstrated that oleate-capped ZnO nanoparticles can be deposited along with a polyethylene-like organic component. The roughness of the obtained surface is important with advancing and receding water contact angles higher than 160°. The roughness is controlled by the deposition time and the nanoparticles concentration in the dispersion.

[0003] However, the obtained coating does not fully cover the substrate and cannot afford corrosion protection to the substrate surface.

[0004] Boscher N. D. et al., (study entitled "Atmospheric pressure plasma polymerisation of metalloporphyrins containing mesoporous membranes for gas sensing applications" in Surf. Coat. Technol., 2013, 234, 48-52 and in European Patent numbered EP 2546636 B1) have demonstrated that an atmospheric pressure plasma route toward the formation of smart mesoporous coatings. The formation of a gas sensing porphyrin-based hybrid coating by an atmospheric pressure dielectric barrier discharge (AP-DBD) fed with nitrogen is thus reported. This is a liquid-assisted plasma-enhanced chemical vapour deposition for forming a porous colorimetric gas sensing layer.
Boscher N. D. et al., (study entitled "Luminescent lanthanide-based hybrid coatings deposited by atmospheric pressure plasma assisted chemical vapour deposition" in J. Mater. Chem., 2011, 21, 18959-18961) have demonstrated an atmospheric pressure plasma route toward the formation of smart hybrid coatings. The formation of a luminescent lanthanide-based hybrid coating by an atmospheric pressure dielectric barrier discharge (AP-DBD) fed with synthetic air is thus reported. A suspension composed of optically active lanthanide-containing coordination polymer particles, a silica matrix forming precursor (hexamethyldisiloxane) and a solvent (e.g. ethanol) is sprayed onto the surface of a substrate (aluminium or polypropylene foil) with an ultrasonic nebuliser. Then, the deposited layer is polymerized by AD-DBD treatment to form a composite coating which is adherent to the substrate and has a thickness of 500 nm. This composite coating is transparent to visible light but emit a strong green colour under UV irradiation (302 nm). Such luminescent hybrid coating is useful to label materials in which the anticounterfeiting particles cannot be directly embed due to high forming temperature employed.

The use of a solvent favours the formation of pores during exposition with the plasma.

International patent application published WO 2009/086161 A1 describes a method of forming an article comprising a network-like pattern of conductive traces formed of at least partially joined nanoparticles defining random-shaped cells transparent to light. In the described article, at least a portion of the cells are at least partially filled with a transparent filler material that can be electrically conductive and/or that can provide protection properties against moisture and oxygen. The described method comprises the steps of (a) applying a liquid emulsion comprising a continuous phase with electrically conductive nanoparticles to the surface of a substrate, (b) drying the emulsion to remove the solvent and subsequently forming a transparent electrically conductive coating and (c) applying a transparent filler material.

The knowledge of the prior art allows to provide multi-layered coating that can be electrically conducting (by choosing the right particles to be
coated). However, even if further particles with anti-corrosive properties can be added, the method of forming the multi-layered coating still uses a solvent that has to be removed (for example by evaporation) and thus can potentially create a defect into the surface. In general, the surfaces obtained by the known methods can be electrically conductive but they cannot afford an important level of anti-corrosive properties. Moreover, quite often, high temperatures are required in order to remove the solvent. This can be a drawback for certain type of substrate.

Summary of invention

Technical Problem

[0009] The invention has for technical problem to alleviate at least one of the drawbacks present in the prior art. More particularly, the invention has for technical problem to provide a fast and one-step method that forms a coating which is electrically conductive with anti-corrosion properties.

Technical solution

[0010] The invention is directed to a method for forming an electrically conductive multi-layer coating with anti-corrosion properties and with a thickness comprised between 1 µm and 10 µm onto a substrate, said method comprising the following subsequent steps of (a) providing a suspension consisting of electrically conductive fillers into a matrix forming material; (b) depositing said suspension on at least a surface portion of a substrate; (c) exposing an atmospheric pressure plasma to said surface portion so as to form one electrically conductive layer with anti-corrosion properties; and (d) repeating said steps (a), (b) and (c). Said method is remarkable in that said electrically conductive fillers are electrically conductive particles.

[0011] According to a preferred embodiment, said electrically conductive particles have dimensions between 0.1 µm and 10 µm, or with dimensions between 0.1 µm and 50 µm, or with dimensions between 0.1 µm and 100 µm.

[0012] According to a preferred embodiment, said electrically conductive particles have an average diameter size below 50 nm and/or below 25 nm.
According to a preferred embodiment, said electrically conductive particles with dimensions between 0.1 µηη and 10 µηη, or with dimensions between 0.1 µηη and 50 µηη, or with dimensions between 0.1 µηη and 100 µηη, are one-dimensional particles or two-dimensional particles.

According to a preferred embodiment, said electrically conductive particles have dimensions between 0.1 µηη and 5 µηη.

According to a preferred embodiment, said electrically conductive fillers further comprise electrically conductive particles with dimensions between 1 nm and 99 nm.

According to a preferred embodiment, said electrically conductive particles with dimensions between 1 nm and 99 nm are three-dimensional particles.

According to a preferred embodiment, said electrically conductive particles with dimensions between 0.1 µηη and 10 µηη, or with dimensions between 0.1 µηη and 50 µηη, or with dimensions between 0.1 µηη and 100 µηη, have a size superior to the thickness of each layer formed by steps (a), (b) and (c).

According to a preferred embodiment, said thickness of a layer is comprised between 5 nm and 100 nm, preferentially between 5 nm and 25 nm.

According to a preferred embodiment, said method further comprises the step of repeating steps (a), (b) and (c) multiple times to control the thickness of said electrically conductive coating with anti-corrosion properties, steps (a), (b) and (c) being preferentially repeated one hundred times.

According to a preferred embodiment, said step (d) is repeated at least once, preferentially at least fifty times, more preferentially one hundred times.

According to a preferred embodiment, said electrically conductive multi-layer coating with anti-corrosion properties has a thickness comprised between 2 µηη and 5 µηη.

According to a preferred embodiment, said electrically conductive coating with anti-corrosion properties is formed by a stacking at least two layers, each layer being composed of both electrically conductive particles with
dimensions between 0.1 \( \mu m \) and 10 \( \mu m \), or with dimensions between 0.1 \( \mu m \) and 50 \( \mu m \), or with dimensions between 0.1 \( \mu m \) and 100 \( \mu m \), and electrically conductive particles with dimensions between 1 nm and 99 nm, the length of said electrically conductive particles with dimensions between 0.1 \( \mu m \) and 10 \( \mu m \), or with dimensions between 0.1 \( \mu m \) and 50 \( \mu m \), or with dimensions between 0.1 \( \mu m \) and 100 \( \mu m \), being superior to the thickness of said each layer.

[0023] According to a preferred embodiment, the volume fraction of electrically conductive particles with dimensions between 0.1 \( \mu m \) and 10 \( \mu m \), or with dimensions between 0.1 \( \mu m \) and 50 \( \mu m \), or with dimensions between 0.1 \( \mu m \) and 100 \( \mu m \), in the electrically conductive coating with anti-corrosion properties is comprised between 50 \% and 85 \%.

[0024] According to a preferred embodiment, the volume fraction of electrically conductive particles with dimensions between 1 nm and 99 nm in the electrically conductive coating with anti-corrosion properties is equal or less than 25 \%.

[0025] According to a preferred embodiment, said electrically conductive particles with dimensions between 0.1 \( \mu m \) and 10 \( \mu m \), or with dimensions between 0.1 \( \mu m \) and 50 \( \mu m \), or with dimensions between 0.1 \( \mu m \) and 100 \( \mu m \), and electrically conductive particles with dimensions between 1 nm and 99 nm are based on graphene and/or graphite.

[0026] According to a preferred embodiment, the matrix forming material is based on a first organosilicon compound, preferentially a first siloxane compound, more preferentially vinyltrimethoxysilane.

[0027] According to a preferred embodiment, the average diameter of said electrically conductive particles with dimensions between 1 nm and 99 nm is comprised between 5 nm and 50 nm.

[0028] According to a preferred embodiment, said atmospheric pressure plasma is composed of nitrogen gas and/or oxygen gas and/or a second organosilicon compound, preferentially a second siloxane compound, more preferentially octamethylcyclotetrasiloxane.

[0029] According to a preferred embodiment, said substrate is a metallic substrate, preferentially a plate of titanium.
According to a preferred embodiment, the suspension of step (a) is sonicated for one hour before step (b).

According to a preferred embodiment, said step (c) is performed at a temperature comprised between 5°C and 90°C, preferably between 15°C and 40°C.

According to a preferred embodiment, the metallic substrate is provided on a moving stage transporting the substrate through a suspension deposition zone to deposit the suspension on at least a portion of the substrate and a plasma zone in which the atmospheric pressure plasma is applied.

According to a preferred embodiment, the moving stage is adapted to move the substrate repeatedly through the zones.

In general, the particular embodiments of each object of the invention are also applicable to other objects of the invention. To the extent possible, each object of the invention is combinable with other objects.

Advantages of the invention

The invention is particularly interesting in that it provides a method for forming a multi-layered coating presenting both electrically conductive and anti-corrosion properties. The use of plasma allows the rapid and simultaneous synthesis and deposition of the coating onto the metallic substrate. Indeed, with the use of plasma, the coating formation is measured in terms of seconds. As no solvent is used, there is no need to remove it and no waste is created. In addition, the coating formation is undertaken at room-temperature and atmospheric-pressure. There is no need to use relatively high temperature nor to operate under vacuum. All these conditions allow the deposition of a conductive coating, which will not corrode, even after more than 100 hours of chronoamperometry test under harsh conditions. Obtaining of homogeneous coated surface is reached, such surface being preventing of any defects.
Brief description of the drawings

[0036] Figure 1 shows a schematic perspective view of an apparatus for carrying out the method according to the present invention.

[0037] Figure 2 shows a plot of the electrically conductivity in function of the carbon-based conductive filler volume fraction.

[0038] Figure 3 shows top-view secondary electron microscopy (SEM) images of electrically conductive composite coatings elaborated from different conditions and employing carbon-based conductive fillers.

[0039] Figure 4 shows side-view secondary electron microscopy (SEM) images of electrically conductive composite coatings elaborated from different conditions and employing carbon-based conductive fillers.

[0040] Figure 5 shows chronoamperometry curves in order to determine the anti-corrosion properties of the obtained multilayer coating.

[0041] Figure 6 shows the optical images of the electrically conductive composite coating elaborated from different deposition conditions prior and after 8 hours of chronoamperometry test.

[0042] Figure 7 illustrates one layer obtained according to the method of the invention, with large and small electrically conductive fillers.

[0043] Figure 8 shows the formation of the multi-layered coating on the metallic substrate, in accordance with the method of the invention.

Description of an embodiment

[0044] Figure 1 shows a schematic view of an exemplary system for carrying out the invention. According to figure 1, a suspension 2 consisting of electrically conductive fillers into a matrix forming material is deposited onto a portion of one substrate 4. No solvent whatsoever is present in the suspension 2. The liquid form of the suspension 2 is due to the matrix forming material. A stage 6 transports the substrate 4 into the direction x such that the portion of the substrate 4 is moved through a plasma zone 8 in which the coated substrate is exposed to an atmospheric pressure dielectric barrier discharge (AP-DBD) plasma 8. Both zones do not overlap, or are spatially distinct, respectively. The dielectric barrier discharge is provided via a system of two electrodes 10 arranged side by
side and having a slot between them through which a gas G may pass to be directed in the direction of the coated substrate 4. Both electrodes 10 are coated with a dielectric layer 12. Being exposed to the dielectric barrier discharge plasma, the matrix forming material forms a solid layer embedding the electrically conductive fillers on the substrate 4. Having passed the plasma zone 8, the substrate 2 comprises a layer 14 including the electrically conductive fillers. Although not depicted, the above-mentioned steps should be carried out several times in order to obtain an effective multi-layered coating. Furthermore, the method is carried out at atmospheric pressure, i.e. at pressures of about 10^5 Pa and at relatively low temperature, for example between 5°C and 90°C, preferably between 15°C and 40°C.

[0045] In particular, it is possible that the moving stage 6 is arranged as a conveyor belt so that the metallic substrate 2 can in principle pass endlessly through the zones of the system.

[0046] Alternatively, the mentioned zones could be adapted to repeatedly pass over the substrate. A further variant consists in repeating sequences of depositing the suspension and/or applying the plasma to a production line.

[0047] Numerous electrically conductive fillers, including metallic or non-metallic core particles, have been investigated. Carbon-based electrically conductive fillers are of particular interest due to their physical and chemical properties. They can be indeed more robust than steel, lighter than aluminium, more conductive than copper and less prone to corrosion than most metals or metal alloys. Among the carbon-based electrically conductive fillers, the following can be used: carbon black, carbon fibres, synthetic or natural graphite, graphene, carbon nanotube including multi-walled carbon nanotubes (MWCNTs). Examples of commercially-available carbon-based conductive fillers are: Timrex® SFG6, C-NERGY™ Super C65, Ketjenblack EC300J, Vulcan XC72R, Ketjenblack EC330JMA, Ketjenblack EC600JC, C-NERGY™ Super C45, Conductex 975 Ultra, Shewinigan Black, Timrex® KS6, SUPER P Li, C-NERGY™ SFG6L, C-NERGY™ KS6L, Raven®, Raven® 1220 Ultra®, Raven® 1250, Raven®
Matrix-forming material can be polymer-forming material. Plethora of matrix or binder materials has been investigated for the formation of electrically conductive composite coatings. The careful selection of the matrix or binder materials may provide additional properties to the resulting conductive composite material. Various corrosion resistant matrices have been successfully investigated, including polytetrafluoroethylene (PTFE), polypropylene (PP), polyphenylene sulphide (PPS), phenolic resins, polyvinylidene fluoride (PVDF), siloxane, vinyl ester resins.

Substrates can be metallic substrates, for instance a plate of titanium, substrates in paper, in wood, in glass, in polymer, in cellulose, etc.

More particularly, a suspension composed of carbon black nanoparticles, *e.g.* Ketjenblack EC600JC, and a siloxane precursor as the matrix forming material, *e.g.* vinyltrimethoxysilane (VTMOS), is deposited as a thin liquid layer, *ca.* hundreds of nanometres, onto a metallic substrate, for instance, a plate of titanium. Subsequently, the coated substrate, placed on the grounded electrode of an atmospheric-pressure dielectric barrier discharge (AP-DBD) setup, is exposed to an AP-DBD ignited by a 10,000 Hz sinusoidal electrical excitation of 8,000 V. The plasma discharge gas is composed of nitrogen, oxygen and vapours of a second siloxane precursor, *e.g.* octamethylcyclotetrasiloxane (OMCTS). The suspension deposition step and the plasma curing step, (*i.e.* the deposition cycle), may be repeated multiple times to achieve electrically conductive composite coatings with the desired thickness. In the present example, fifty deposition cycles are performed. As a result of exposure to the AP-DBD, a solid and adherent electrically conductive composite coating is formed on top of the metallic substrate.

The carbon black nanoparticles concentration into the liquid matrix precursor, *i.e.* VTMOS, is varied between 0.5 to 10 g·L⁻¹, allowing to investigate various carbon-based electrically conductive fillers volume fraction, *i.e.* 10 to 40 %, in the resulting composite coating. Two different
conductive fillers, with average diameter size below 50 nm and 25 nm, were also investigated. The resulting composite coatings are shown to follow the percolation theory. This theory consists in a sharp increase of the conductivity, from several orders of magnitude, when the volume fraction of conductive fillers exceeds a critical value, i.e. the percolation threshold (see figure 2). Following to this rapid increase of the conductivity, no significant changes in the electrical properties of the composite coatings are observed anymore.

[0052] It is to be noted that the volume fraction of the electrically conductive carbon-based particles is determined by energy-dispersive X-ray spectroscopy (EDX), since the liquid matrix-forming material is volatile and the concentration of the suspension can be different from the formed electrically conductive multi-layer coating.

[0053] Sample A, which is a sample with a low volume fraction, has a specific contact resistivity of 130,000 mΩ-cm². In other words, sample A is poorly electrically conductive.

[0054] When the volume fraction increases, as shown in figure 2, the percolation threshold is reached and thus, samples B to E reaches the plateau with a minimum specific contact resistivity of 10 mΩ-cm², therefore with an increased electrical conductivity.

[0055] However, an increase of the carbon-based electrically conductive fillers volume fraction above a certain value, i.e. 25 %, results in the formation of powdery and non-adherent coatings. Corrosion problems start to appear above the plateau shown in figure 2.

[0056] That is the reason why the ratio of electrically conductive particles with dimensions between 1 nm and 99 nm in the coating is equal or less than 25 %.

[0057] Additional investigations have demonstrated that this maximum volume fraction is higher for composite coatings elaborated from the bigger carbon-based conductive fillers, e.g. Ketjenblack EC330JMA. In accordance with previous research works, the percolation threshold is reached with a lower fraction of carbon-based conductive fillers for the
composite coatings elaborated from the highest specific surface area carbon-based conductive fillers.

[0058] Scanning electron microscopy (SEM) (see figure 3) shows that the electrically conductive composite coatings cover the whole surface of the metallic substrate. The electrically conductive composite coatings with the lowest carbon-based conductive fillers volume fraction, i.e. condition A, exhibit a dense morphology with carbon-based conductive fillers present at all over their surface.

[0059] Composite coatings prepared from a volume fraction above the conductivity percolation threshold (conditions B to E) show a large number of spherical carbon-based conductive fillers, seemingly laced together to form necklaces. The observed necklaces appear thinner as the volume fraction of carbon-based conductive fillers increase.

[0060] The thickness of the electrically conductive composite coatings grown from fifty deposition cycles, determined from Scanning Electron Microscopy (SEM) side-view observations (see figure 4), is shown to fluctuate from 1 to 10 \( \mu \)m, or more often from 2 to 5 \( \mu \)m, irrespective of the deposition conditions. This allows the use of such multilayer coating in order to make bipolar plates for fuel cell application. Interesting electrical properties can be demonstrated when such a low thickness is provided to a substrate.

[0061] Indeed, the low thickness of the multi-layer coating, i.e. comprised between 1 \( \mu \)m and 10 \( \mu \)m, allows for a material which is functionalized with such electrically conductive multi-layer coating with anti-corrosion properties to display a high electrically conductance \( G \). This provides an increase of the electrical intensity \( I \) during electrical connection.

[0062] Chronoamperometry tests have been provided to determine the anti-corrosion properties of the multi-layered coating obtained according to the method of the invention.

[0063] The corrosion tests are carried out in a conventional corrosion cell \( (V = 300 \text{ ml}) \) coupled to a GAMRY 600 potentiostat. The corrosion test conditions are chosen to simulate a fuel cell operation conditions. The electrolyte composition is as following: \( \text{pH} = 3 \) (H\(_2\)SO\(_4\)); \( \text{Cl}^- \) 10 ppm (NaCl) and \( \text{F}^- \) 30 ppm (NaF). The chronoamperometry parameters are the
following: the voltage is set up to 0.9 V vs SHE; the electrolyte temperature 80°C and the duration of the tests is 100 hours. These conditions are actually quite harsh conditions in order to obtain a relevant idea of the anti-corrosion properties of the coated substrates.

[0064] Figure 5 shows that all the electrically conductive composite coatings ensure a reduction of the corrosion current.

[0065] The corrosion performances are shown to be inversely related with the volume fraction of conductive fillers. This result is consistent with the observations made by SEM as denser layers are expected to provide a far better protection. Samples A and B did allow to maintain the corrosion current to 0.25 µA·cm² for several hours. However, delamination occurred on several places and led to a rapid increase of the corrosion current after three hours under the test conditions.

[0066] Interestingly, condition B, which is already above the percolation threshold, provides a significant corrosion protection to the metallic substrate.

[0067] This highlights the suitability of the proposed approach for the deposition of electrically conductive composite coatings for the preparation of fuel cell bipolar plates.

[0068] For conditions C to E, the numerous voids within the electrically conductive composite coatings induce lower corrosion properties of the films. Nevertheless, contact resistance measurements performed after the eight hours chronoamperometry test show an unaltered or barely altered contact resistance (i.e. tens of mΩ·cm²).

[0069] Therefore, these deposition conditions are also very interesting in the preparation of bipolar plates for fuel cell application.

[0070] Additionally, optical and SEM observations of the electrically conductive composite coatings after the corrosion test did not reveal any change of the morphology of the film in relation with sample E (see figure 6). These results indicate the excellent behavior of the electrically conductive composite coatings when exposed to the fuel cell operating conditions.

[0071] Several literature works have reported an increase of the in-plane and through-plane conductivities with increasing size of the electrically conductive fillers (typically in the micrometre to tens of micrometres
range). Indeed, the use of small conductive fillers is assumed to unproductively multiplicate the conductive pathway disruptions, increasing the contact resistance, and the structure defects, which gut the corrosion properties of the electrically conductive composite coatings. In addition, the shape of large conductive fillers is an important parameter. 1D (e.g. fibres, nanotubes) or 2D conductive materials (e.g. flakes) have notably been reported to confer better properties to the conductive and corrosion-resistant composite coatings than 3D conductive materials. Graphite flakes (2D) and carbon fibres (1D) effectively stacked to form effective conductive pathways. On the other hand, large 3D conductive fillers form large voids, which are detrimental to both the contact resistance and corrosion resistance.

[0072] A further improvement of the electrical conductivity and corrosion performances of the electrically conductive composite coatings is the use of smaller conductive fillers in complement to the large conductive fillers. The small fillers, filling the voids formed by the large fillers, can significantly improve the electrical conductivity of the composite coatings. One should be aware that the small conductive fillers size should be well below the large conductive fillers size to adequately fill the voids and form proper conductive pathways.

[0073] In general, it has been experimented that the large conductive fillers are particles with dimensions comprised between 0.1 μm and 100 μm while the smaller conductive fillers are particles with dimensions comprised between 1 nm and 99 nm.

[0074] The particles may be of one-dimensional shape, two-dimensional shape and/or three-dimensional shape, the particles with dimensions comprised between 1 nm and 99 nm being preferentially three-dimensional particles.

[0075] The particles with dimensions comprised between 0.1 μm and 100 μm, advantageously with dimensions comprised between 0.1 μm and 50 μm, have a size which is superior to the thickness of each layer which is comprised between 5 nm and 100 nm, preferentially between 5 nm and 25 nm. As the particles within one layer overtake the surface of said layer, the
electrical conductivity between two adjacent layers is considerably enhanced.

[0076] It is to be noted that the dimensions of the carbon-based particles have been determined by Scanning Electron Microscopy (SEM) and are in fact the expression of D50 (medium value of the particle size distribution).

[0077] Both electrical conductivity and corrosion performances of the electrically conductive composite coatings are improved by simultaneously employing large 1D or 2D electrically conductive fillers and small 3D electrically conductive fillers. Figure 7 shows such how such coating can be illustrated, while figure 8 shows the formation of the multi-layered coating on a substrate 4.

[0078] On one hand, the large electrically conductive fillers, made of natural graphite flakes with a 2D shape and a size in the micrometer range (for instance, Micro850 from Asbury Carbons), have been selected as the major electrically conductive filler with loading content from 50 to 85 %. Preferably, the large conductive fillers are thus in excess in comparison to the smaller conductive fillers.

[0079] On the other hand, the smaller electrically conductive fillers, with a 3D shape and a 6 nm size (for instance, Ketjenblack EC600JC), have been selected as minor conductive filler with loading content from 0 to 25 %.

[0080] The two types of electrically conductive fillers have been dispersed in the matrix precursor, e.g. a monomer with free-radical polymerisable bonds, and sonicated for one hour.

[0081] A thin layer of the polydisperse suspension is subsequently applied on the surface of the metallic substrate to be coated and briefly exposed to an atmospheric-pressure plasma discharge. The thickness of the deposited liquid and polydisperse suspension layer is in the range of several tens to several hundreds of nanometers, which is lower than the longest dimension of the major filler.

[0082] A total of ten deposition cycles is performed in order to mitigate the defects of each deposition cycle. As a result to this sequence, a plurality of stacked electrically conductive composite layers constituting an electrically conductive composite coatings coating are formed.
The resulting electrically conductive composite coating exhibits both a high electrical conductivity and corrosion-protection properties.

It is worth to note that the multi-layer coating obtained according to the present invention can be coated on other substrate 4 than the metallic substrate on which the exemplary embodiment has been described. For instance, substrate 4 such as paper, wood, cellulose, polymer or glass could be used.
Claims

1. Method for forming an electrically conductive multi-layer coating with anti-corrosion properties and with a thickness comprised between 1 µm and 10 µm onto a metallic substrate (4), said method comprising the following subsequent steps:
   a) providing a solvent-free suspension with electrically conductive fillers into a liquid matrix-forming material;
   b) depositing said suspension on at least a surface portion of a metallic substrate;
   c) exposing an atmospheric pressure plasma to said surface portion so as to form one electrically conductive layer with anti-corrosion properties; and
   d) repeating said steps (a), (b) and (c);
characterized in that said electrically conductive fillers are electrically conductive carbon-based particles.

2. Method according to claim 1, characterized in that said electrically conductive carbon-based particles have dimensions between 0.1 µm and 50 µm.

3. Method according to claim 2, characterized in that said electrically conductive carbon-based particles with dimensions between 0.1 µm and 50 µm are one-dimensional carbon-based particles or two-dimensional carbon-based particles.

4. Method according to any one of claims 1-3, characterized in that said electrically conductive carbon-based particles have dimensions between 0.1 µm and 5 µm.

5. Method according to any one of claims 1-4, characterized in that said electrically conductive fillers further comprises electrically conductive
carbon-based particles with dimensions between 1 nm and 99 nm, said carbon-based particles with dimensions between 1 nm and 99 nm being preferentially three-dimensional carbon-based particles.

6. Method according to any one of claims 2-5, characterized in that said electrically conductive carbon-based particles with dimensions between 0.1 \( \mu \text{m} \) and 50 \( \mu \text{m} \) have a size superior to the thickness of each layer formed by steps (a), (b) and (c).

7. Method according to claim 6, characterized in that the thickness of a layer is comprised between 5 nm and 100 nm, preferentially between 5 nm and 25 nm.

8. Method according to any one of claims 1-7, characterized in that said electrically conductive multi-layer coating with anti-corrosion properties has a thickness comprised between 2 \( \mu \text{m} \) and 5 \( \mu \text{m} \).

9. Method according to any one of claims 2-8, characterized in that the volume fraction of electrically conductive carbon-based particles with dimensions between 0.1 \( \mu \text{m} \) and 50 \( \mu \text{m} \) in the electrically conductive coating with anti-corrosion properties is comprised between 50 % and 85 %.

10. Method according to any one of claims 5-9, characterized in that the volume fraction of electrically conductive carbon-based particles with dimensions between 1 nm and 99 nm in the electrically conductive coating with anti-corrosion properties is equal or less than 25 %.

11. Method according to any one of claims 2-10, characterized in that said electrically conductive carbon-based particles with dimensions between 0.1 \( \mu \text{m} \) and 50 \( \mu \text{m} \) and electrically conductive carbon-based particles with
dimensions between 1 nm and 99 nm are based on graphene and/or graphite.

12. Method according to any one of claims 1-11, characterized in that said liquid matrix-forming material is based on a first organosilicon compound, preferentially a first siloxane compound, more preferentially vinyltrimethoxysilane.

13. Method according to any one of claims 5-12, characterized in that the average diameter of said electrically conductive carbon-based particles with dimensions between 1 nm and 99 nm is comprised between 5 nm and 50 nm.

14. Method according to any one of claims 1-13, characterized in that said atmospheric pressure plasma is composed of nitrogen gas and/or oxygen gas and/or a second organosilicon compound, preferentially a second siloxane compound, more preferentially octamethylcyclotetrasiloxane.

15. Method according to any one of claims 1-14, characterized in that said metallic substrate is a plate of titanium.

16. Method according to any one of claims 1-15, characterized in that the suspension of step (a) is sonicated for one hour before step (b).

17. Method according to any one of claims 1-16, wherein said step (c) is performed at a temperature comprised between 5°C and 90°C, preferably between 15°C and 40°C.

18. Method according to any one of claims 1-17, characterized in that the
metallic substrate is provided on a moving stage transporting the metallic substrate through a suspension deposition zone to deposit the suspension on at least a portion of the metallic substrate and a plasma zone in which the atmospheric pressure plasma is applied.

19. Method according to claim 18, wherein the moving stage is adapted to move the metallic substrate repeatedly through the zones.
Fig. 5

Fig. 6
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. B05D5/12 B05D1/38 C09D5/08 C09D5/24 H01B1/24
ADD.

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)
B05D C23C C08L C09D H01B H01M

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)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>JULIEN BARDON ET AL: &quot;Di spersi on of Ceri um-Based Nanoparti cles in an Organosi 1i con Plasma Polymeri zed Coati ng: Effect on Corrosi on on Protecti on&quot;, PLASMA PROCESSES AND POLYMERS, vol. 6, no. 1, 26 May 2009 (2009-05-26) ; pages S655-S659, XP055383368, DE ISSN: 1612-8850, DOI: 10.1002/ppap. 200931710 abstract; figure 1</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search: 7 February 2018

Date of mailing of the international search report: 20/02/2018

Authorized officer: Mei ners, Chri stian
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<td>US 2012/003449 AI (YIALIZIS ANGELO [US] ET AL) 5 January 2012 (2012-01-05) abstract paragraph [0027]; claims 17,20; example 1</td>
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