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(54) **Title**: PROCESS FOR DEPOSITING METAL ON ONE OR MORE SUBSTRATES, COATED SUBSTRATE, AND USE THEREOF

(57) **Abstract**: The invention relates to a MOCVD process for coating of one or more substrates with a metal such that the coating is essentially free of surface defects, wherein the substrates are supported in a CVD apparatus and brought into contact with metal-organic compound-containing chemical vapour which decomposes to form the metal coating on the substrate essentially free of surface defects. The process comprises two or more coating steps wherein the substrate(s) is/are essentially not in motion in relation to one another and/or the support,and one or more movement steps wherein the substrate(s) is/are in motion in relation to one another and/or the support,with at least part of the metal, preferably most of the metal, being deposited during the coating steps.

PROCESS FOR DEPOSITING METAL ON ONE OR MORE SUBSTRATES, COATED SUBSTRATE, AND USE THEREOF

The invention relates to a process for depositing metal on one or more substrates. It furthermore relates to the resulting coated substrate and to the use of such coated substrates.

Many metal substrates, such as fasteners, screws, nails, rivets, metal sheets, automobile parts, and the like, are coated with metallic coatings to make them corrosion resistant and improve their ability to withstand media such as chlorine, demineralized water, seawater, biodiesel, alcohol, fuel, cooling fluids, etcetera. Various techniques are known in the art for deposition of metal films on metal substrates. One example of such a process is physical vapour deposition (PVD), a technique used in the art to deposit thin metal films onto various surfaces by physical means, which can be performed in various ways - for instance by sputtering. It requires extensive deposition equipment which is difficult to operate and maintain. Also, for PVD typically a vacuum and/or plasma-treatment is required, making it less suitable for continuous operations or operations wherein the batch times should be short (less than 30 minutes per batch). Further, because sputtering is a technique wherein metal is vaporized locally and the metal vapour travels towards the substrate, the substrate has to be in constant motion if it is to be coated in three dimensions. Other ways of depositing thin metal films on substrates are via galvanic metal deposition, sheradizing, or by dipping substrates into a molten metal.
It was found, however, that such deposition methods give poor control over the adherence of the metal coating to the substrate and the formation of alloys, as well as poor layer structure and a deposited layer thickness that is difficult to control.

Metal-Organic Chemical Vapour Deposition (MOCVD) is another technique used in the art to deposit thin metal films on substrates. In a typical MOCVD

process, the substrate is exposed to one or more, preferably gaseous, metal-containing precursors, which react and/or decompose on the substrate surface to produce the desired metal deposit. An advantage of a MOCVD deposition process compared to non-CVD alternative metal coating methods is that the MOCVD process allows for the effective coating of complex shapes with small features and patterns, such as openings, crevices, lines, dents, dimples, pits, and indentions, as well as the internal surfaces of objects such as pipes or inner threads. This is largely due to the precursor being in the vapour phase, which makes it possible to approach all of the substrate's surfaces.

A MOCVD method for depositing a substantially pure, conformal metal layer on substrates in bulk quantities through the decomposition of a metal-containing precursor is described in WO 2005/028704. During the described deposition process, the substrates are maintained at a temperature higher than the decomposition temperature of the precursor, while the surrounding gas is maintained at a temperature lower than the decomposition temperature of the precursor. This technology is elaborated upon in WO 2011/012636, which shows that by using a temperature profile during coating it is possible to create a multi-zone layer of metal on a substrate. This process for making a multi-zone layer is characterized in that first a temperature is applied that is below the melting temperature of the substrate but above the temperature at which the coating metal is generated from the precursor and diffuses into the substrate, after which the temperature is lowered to a temperature at which the metal is mainly deposited onto the surface. In both processes the substrates are typically metallic parts that are treated batchwise. Both processes result in a coating with excellent adhesion and providing excellent corrosion resistance of the substrate. Also, the processes allow for continuous operations with a residence time of the substrate of 120, 60, and more preferably less than 30 minutes or, alternatively, batch operations with batch times of less than 180 minutes, preferably less than 120, more preferably less than 60, and most preferably less than 30 minutes.

When practising the technology of WO 2005/028704 and WO 2011/012636, particularly when more substrates were coated simultaneously in the same batch, the substrates were kept in motion when contacted with a chemical vapour from which metal was deposited, in order to obtain a uniform coating of the substrate. As mentioned in WO 2011/012636, good adhesion of the coating to the substrate was observed and a minimal presence was found of positive throwing power defects (edges thickening) or of defects where base material is exposed (not fully coated) when coating more substrates simultaneously. However, on smooth surfaces there are still undesired surface defects. The process of WO 2005/028704 was found to similarly result in defects on flat surfaces. These defects typically show as minute lumps on, or dents in, the surfaces of the coated substrate and they are not thickened edges or defects wherein base material (substrate) is exposed.

It is an object of the present invention to improve the prior art MOCVD process wherein one or more substrates are coated, by reducing the amount of surface defects while maintaining the excellent adhesion of the coating layer and the excellent corrosion resistance previously achieved. Furthermore, it is an object of the present invention to provide a straightforward and time-efficient process for preparing such a metal-coated substrate.

It was found that the objects of the present invention are realized by adapting process conditions. In more detail, it was found that in order to get the required coating layer with less defects, preferably a layer that is essentially free of surface defects, it is required to use a MOCVD process wherein the one or more substrates are supported in a CVD apparatus and brought into contact with a metal-organic compound-containing chemical vapour, with the temperature of the substrate causing decomposition of the vapour and deposition of the metal onto the substrate, and wherein said process comprises two or more coating steps wherein the substrate(s) is/are essentially not in motion in relation to one another and/or the support, and one or more

movement steps wherein the substrate(s) is/are in motion in relation to one another and/or the support, with at least part of the metal, preferably most of the metal, being deposited during the coating steps. Preferably, the movement step is between two coating steps.

Accordingly, the invention relates to a metal-organic chemical vapour deposition process wherein one or more substrates are supported in a CVD apparatus and wherein said process comprises two or more coating steps wherein the one or more substrates are brought into contact with a vapour of a metal-organic chemical under conditions such that said metal-organic chemical decomposes and metal is deposited onto the substrate, during which process said substrates are essentially not in motion in relation to one another and/or the support, and one or more movement steps wherein the one or more substrates are in motion in relation to one another and/or the support.

It is to be understood that during the initial phase of the coating process, the substrates are typically heated to the desired temperature. Generally, the substrate is in motion during this heating phase in order to equalize the temperature of the substrates. In the conventional processes, the substrate was typically kept in motion during subsequent coating stages to get an even distribution of the coating. However, as said, even when it was kept in motion, surface defects were still observed.

There are various unproven theories for the cause of defects on the surface. One is that due to the movement while coating, a substrate will bump into another substrate or into the surface of the equipment when the depositing takes place, causing local temperature differences, resulting in differences in the deposition rate of the metal. Another is that substrates are glued together during metal deposition, the bond breaking at the substrate-metal layer due to motion, resulting in locally thicker and thinner metal layers.

However, even when the substrate is coated without being kept in motion, various surface defects are observed. According to another theory, this is due to

the fact that the part of the substrate that is in contact with another substrate or with the surface of the equipment will not be coated by the metal at and near the contact area.

Since surface defects were found to be more frequent in a process where a large number of substrates are coated simultaneously, the process of the invention is particularly suitable for simultaneously coating multiple substrates. Hence, in an embodiment of the invention, the number of substrates coated simultaneously in a coating step of the process is greater than 2, preferably greater than 10, more preferably greater than 50.

Another embodiment the invention relates to the coating of less than 10, preferably less than 5 substrates, with the volume taken up by the substrate being more than 50% of the internal volume of the CVD equipment in which the coating is performed, because in such a situation there is frequent contact between the substrate and the support and walls of the CVD equipment if the substrate is kept in motion.

In a further embodiment, where the coating is part of a continuous operation, it is possible to avoid surface defects by minimizing deposition of the metal during movement of the substrate relative to the support or other substrate.

The surface defects as mentioned herein are defined as a visual unevenness in the coating layer surface, as determined by light microscopy at a magnification of 200x, where the unevenness has a size of more than 10 micrometers by 10 micrometers and less than 2 mm^2 and this unevenness is due to a coating layer thickness that is at least 15% more or less than the average thickness of the coating layer on the substrate. To avoid any doubt, areas where bare substrate is observed are not surface defects as defined herein. Also edge thickening, where edges of the substrate show more than average coating with metal, are not surface defects as defined herein. It is noted that the average layer thickness is determined by gravimetric analysis of the coated and the uncoated substrate, giving the total amount of coating metal, and calculated by dividing

the amount by the specific density of the metal and dividing by the known surface area of the substrate.

In an embodiment of the invention, multiple substrates are simultaneously subjected to a coating process wherein the substrates are supported in a CVD apparatus and brought into contact with metal-organic compound-containing chemical vapour, with at least a coating step a) wherein the multiple substrates are essentially not in motion and subjected to a metal-organic compound-containing chemical vapour, with the metal-organic compound in said vapour being decomposed in order to deposit the metal of said metal-organic compound onto the substrate, a movement step b) wherein the substrates are put in motion in relation to each other and the support and walls of the CVD equipment, with essentially no metal being deposited, and a coating step c) wherein the multiple substrates are essentially not in motion and again are subjected to a metal-organic compound-containing chemical vapour, with the metal-organic compound in said vapour being decomposed in order to deposit the metal of said metal-organic compound onto the substrate. Preferably, the metal-organic compound of step c) is the same as the metal-organic compound of step a).

It is noted that, if so desired, steps b) and c) may be repeated once, so that the process comprises two steps b and two steps c, or several times, for example to get the desired layer thickness and uniformity. The steps b) and c) are alternated and may be separated by optional further steps. Preferably steps b) and c) are repeated at least twice, more preferably at least three times and more preferably at least four times, to minimize the number of surface defects. If both steps b) and c) are repeated at least once, step a) may be discarded with. An example of a process according to the invention is therefore a process comprising steps a-b-c. In another example it comprises steps a-b-c-b-c. In a further example it comprises steps b-c-b-c. In yet another example it comprises

steps b-c-b-c-b. In further examples, the process would comprise more steps b and c.

In an embodiment of the invention, the process may optionally comprise one or more steps d) wherein the substrate is both in motion and being coated, for instance to optimize the time-space yield of a reactor, and where the number of surface defects is found to be still acceptable, as long as the above identified steps a), b), and c) are present. If such one or more steps d) are involved, they preferably take place in the beginning of the process, such that the steps b) and c) are taken after steps d), to minimize surface defects on the coated substrate.

It is noted that by the term “essentially no metal being deposited” is meant that the deposit rate of the metal onto the substrate is at most 40%, preferably at most 20%, more preferably at most 10%, even more preferably at most 5%, even more preferably still at most 2%, and most preferably at most 1% of the maximum deposit rate during any one of steps a) or c).

Further it is noted that the term “essentially not in motion” in steps a) and c) means that less than 10%, more preferably at most 5%, even more preferably at most 2%, and most preferably at most 1% of all the substrate is moved over a distance of more than the longest dimension of the substrate when it is a particulate and more than the thickness of the material if is a wire, chain, sheet, or single large object, relative to the support of the equipment holding the substrate. Similarly, the term “put in motion” in step b) means that at least 10%, preferably at least 40%, more preferably at least 65%, and most preferably at least 85% of all parts of the substrate that were not exposed to the precursor are moved over a distance sufficient to expose them in a next coating (metallization) step. In practice this means that at least 10%, preferably at least 40%, more preferably at least 65%, and most preferably at least 85% of the substrate is moved over a distance of more than 0.1 mm, preferably more than 0.5 mm, more preferably more than 1 mm, relative to the other substrate and to the support of the equipment holding the substrate.

When saying that preferably most of the metal is deposited in the coating steps, it is meant that at least 50, preferably at least 80, more preferably more than 90%, even more preferably at least 95% of all metal is deposited during the coating steps. If the process includes one or more coating steps during which the substrates are in motion, then the defined coating steps include these steps as well as the coating steps wherein the substrates are not in motion.

In other words, the process is designed such that the deposition of the metal and the motion of the substrates are conducted such that there are steps wherein the substrates do not bump into one another and/or the equipment when the metal is being deposited in the process and at least one other step wherein the deposition is strongly reduced and the substrates are in motion relative to one another and the equipment, so that all surfaces of the substrate will have been exposed to the precursor during the coating steps. These measures were found to strongly reduce or to prevent the formation of surface defects on the coated substrate.

It is to be understood that the step wherein the substrate is put in motion and the steps wherein the coating (metallization) takes place can be combined in such a way that they are consecutive in time, optionally with one or more other steps in between, but they can also take place at the same time, in which case the equipment is such that there are two or more zones, with the step wherein the substrate is in motion and the step wherein the metallization takes place being effected simultaneously in two different zones.

It is further noted that in the one or more steps b) the measure taken to make sure that essentially no metal is deposited can be selected from a large group of measures. Typically, it is accomplished by (1) lowering the temperature to a value at which metal deposition is reduced, in which case there can be precursor (the metal-organic compound of the vapour) in the coating chamber, and/or (2) partial or complete removal of the precursor before the movement of

the substrates is initiated. This can be achieved by flushing the CVD equipment with an inert gas, solvent rinse, evacuation of the gas phase, or similar steps. Also a combination of such measures is possible.

Preferably, the metal of the metal-organic compound in the metal-organic compound-containing chemical vapour is deposited onto the substrate in step a) and one or more steps c) by thermal decomposition of the metal-organic compound.

If desired, the temperature in steps a), c) and/or d) is varied in order to control the diffusion of the deposited metal into the substrate, allowing the formation of a multi-zone coating. Typically, this requires the starting temperature of the substrate to be above the temperature where the diffusion rate of the metal into the substrate is greater than the rate of deposition, but below the melting temperature of the substrate, after which the temperature is lowered such that the deposition rate becomes greater than the diffusion rate of the metal into the substrate.

The process according to the present invention allows multiple substrates to be coated simultaneously, while the adhesion of the metal coating is excellent, particularly for multi-zone coated substrates, the stability in corrosive conditions is excellent, particularly for multi-zone coated substrates, and the coated substrate has excellent properties with respect to contact corrosion, cathodic protection for steel, diffusion barrier properties, such as for hydrogen, the rate of dissolution in media such as chlorine, seawater, demi-water, biodiesel, alcohol, fuel, cooling fluids, etc., weldability and/or stability over a broader pH range, compared to substrates having obtained a coating via conventional methods. Furthermore, the process is very time-efficient.

The substrate to be coated according to the present invention can be any material which is able to withstand the metal-containing precursor used and the

temperatures applied. Preferably, the substrate takes the form of one or more metals and/or alloys.

In an embodiment of the invention, the substrate according to the present invention is a metallic material selected from the group consisting of unalloyed steel, low alloyed steel, high alloyed steel, iron, cast iron, copper, a copper alloy, nickel, a nickel alloy, titanium, a titanium alloy, alpha-titanium, beta-titanium, alpha-beta-titanium, gamma-titanium-aluminium, aluminium, cast aluminium, an aluminium alloy, magnesium, cast magnesium, a magnesium alloy, cobalt, a cobalt alloy, zinc, cast zinc, a zinc alloy, tin, and chromium. Preferably, it is steel.

In another embodiment of the invention, the substrate is a metallized substrate, which is defined here as being pre-coated with a metallic layer on its surface, with the composition of the metallic layer on the surface differing from the composition of the substrate. Preferably, the metal of the metallic layer is selected from the group consisting of zinc, a zinc-nickel alloy, a zinc-iron alloy, a zinc-tin alloy, a zinc-chromium alloy, a zinc-magnesium alloy, a zinc-aluminium alloy, a zinc-aluminium-magnesium alloy, and magnesium, but which is different in composition from the composition of the metallic material. The metallic layer can also be a Galfan® or Galvalume® layer. The metallic layer of the metallized material preferably has a thickness of 0.1 µm up to 1,000 µm, more preferably 0.5 up to 500 µm or even more preferably 1 up to 100 µm. Said metallic layer can be applied using processes such as galvanic, hot-dip, PVD or CVD techniques, or electroplating techniques involving the use of ionic liquids, mechanical deposition, cladding, explosion-cladding, sheradizing, or laser deposition.

Suitable substrates, metallized or not, include small assembly parts, such as fasteners, nuts, bolts, screws, nails, rivets, pins, clamps, ferrules, clips, tags, discs, balls, etc. Also, the suitable substrates can be larger assembly parts, such as (automobile) gearbox parts, (automobile) suspension parts, wheel rims, exhaust manifolds, brake discs, metal sheets. Furthermore, the suitable

substrates include wire, tubes, chains, springs, and metal coil. There is no limitation as to the size of the substrates except for those imposed by the equipment at hand.

The terms "metal-containing precursor" and "metal-organic compound" are used throughout this specification to denote any organometallic compound or organometalloid complex of which it is known in the art that they can be used as MOCVD precursors (see for instance the *Handbook of Chemical Vapour Deposition (CVD), Principles, Technology, and Applications*, 2nd Edition, Hugh O. Pierson, 1999, by Noyes Publications / Willian Andrew Publishing, New York, Chapter 4 entitled "Metallo-Organic CVD (MOCVD)".

The metal-containing precursor is preferably selected from the group consisting of metal alkyls, alkyl metal hydrides, metal alkylamides, metal hydride-amine complexes, and volatile organometallics comprising one or more cyclopentadienyl ligands. Preferably, the metal-containing precursor is an aluminium alkyl compound, a zinc alkyl compound, or a magnesium alkyl compound. More preferably, it is an aluminium alkyl compound or a zinc alkyl compound. Most preferred is an aluminium alkyl compound.

Suitable sources for deposition of an aluminium layer include a metal alkyl compound, such as trimethylaluminium, triethylaluminium, dimethylaluminium hydride, tri-n-butylaluminium, triisobutylaluminium, diethylaluminium hydride, diisobutylaluminium hydride, or other trialkylaluminium or alkylaluminium hydride molecules of the formula $R^1R^2R^3Al$, wherein R^1, R^2, and R^3 are branched, straight chain, or cyclic hydrocarbyl ligands or hydrogen (with the proviso that R^1, R^2, and R^3 are not all hydrogen), and wherein the number of carbon atoms in R^1, R^2, and R^3 ranges from C_1 to C_{12}. The chosen ligands may also include those such as isoprenyl which are bifunctional and which bond to two or three aluminium atoms. The selected precursor compositions may contain mixtures of any or all of the above-mentioned species. Preferably, R^1, R^2, and R^3 as described above are selected from the group consisting of ethyl, isobutyl, and hydrogen, with the most preferred compounds being triethyl

aluminium, triisobutyl aluminium, diisobutyl aluminium hydride or mixtures thereof.

Suitable sources for deposition of a zinc layer include dimethyl zinc, diethyl zinc, di-n-butyl zinc, di-isobutyl zinc, and other dialkyl zinc compounds of the formula R^4-Zn-R^5, wherein R^4 and R^5 are branched, straight chain or cyclic hydrocarbyl ligands, and wherein the number of carbon atoms in R^4 and R^5 ranges from C_1 to C_{12}.

Suitable sources for deposition of a magnesium layer include dicyclopentadienyl magnesium, butylethyl magnesium, di-n-octyl magnesium, diphenyl magnesium, and other dialkyl magnesium compounds of the formula R^6-Zn-R^7, wherein R^6 and R^7 are branched, straight chain or cyclic hydrocarbyl ligands, and wherein the number of carbon atoms in R^6 and R^7 ranges from C_1 to C_{12}.

Before step a) of the present process, the multiple, optionally metallized, substrates are heated to the desired temperature. The rate of heating the substrate is preferably at least 1°C per minute. Preferably, the substrate is not heated at a rate higher than 300°C per minute. This step is performed to improve adhesion of the metallic layer to the metallic material in the case of a metallized material, to homogenize the metallic material if it is an alloy, or to degas the metallic material in the case of a cast alloy. Preferably, the metallic material is heated at a rate of between 1 and 200°C per minute to get the best results. The heating can be performed gradually or step by step. In the case of several heating steps, different heating rates can be applied.

If applicable, the ratio of the rate of diffusion of the deposited metal(s) and the metal(s) of the metallic material and/or metallic outer layer to the rate of deposition of the metal(s) deposited by MOCVD is determined by elemental analysis of the generated multi-zone metallic coating as a function of depth. The chemical composition is analyzed by scanning electron microscopy (SEM) outfitted with Energy-Dispersive X-ray spectroscopy detector (EDX). The rate of diffusion is determined to be higher than or equal to the rate of deposition when

the metals of the metallic material, or of its metallic outer layer in the case of a metallized metallic material, are found at the surface of the metallic material. If only metal(s) deposited by MOCVD are found on the surface, the rate of deposition is higher than the rate of diffusion. If a metal-containing precursor is used comprising a metal which is also present in the metallic core and/or the metallic outer layer, the above method cannot be used. Instead, the ratio of the rate of diffusion of the deposited metal(s) and the metal(s) of the metallic core and/or the metallic outer layer to the rate of deposition of the metal(s) deposited by MOCVD is determined by elemental analysis of trace materials present in the metallic core and/or the metallic outer layer.

As the skilled person will recognize, the reaction conditions in the coating steps are dependent on the metal-containing precursor used and the characteristics of the substrate to be coated. Preferably, the substrates are maintained at a temperature higher than the decomposition temperature of the precursor, while the surrounding vapour and/or gas are maintained at a temperature lower than the decomposition temperature of the precursor. Typically, at a given pressure and a given concentration of the precursor in the vapour and/or gas, the temperature of the substrate is controlled to obtain a desired rate of deposition and, if applicable, diffusion of the metal. The maximum temperature that can be used is below the melting point of the substrate or the melting point of the coating layer. A lower temperature of the substrate typically results in a lower deposition rate of the precursor and slower metal deposition. A too low deposition rate of the coating metal is uneconomic. The optimum temperature range of the substrate during the coating steps will be between these two temperatures. For example, when using triethyl aluminium as precursor and steel plated with zinc as substrate, a temperature of at least 320°C, more preferably at least 330°C, and most preferably at least 340°C is suitably used. The temperature of the substrate preferably is at most 400°C, more preferably at most 380°C, and most preferably at most 370°C. For zinc deposition using zinc alkyl compounds, suitable temperatures are generally lower, typically in the

range of 240-340°C. For magnesium deposition using butylethyl magnesium alkyl-based precursors, temperatures above 350-420°C may be necessary.

A number of methods can be used for heating the substrates. More particularly, the substrates can be heated using a direct heating method, an indirect heating method, or a combination of both. By direct heating is meant that the substrate is heated by direct contact between the substrate and the heating source. Examples of direct heating are contacting with a hot inert gas such as a flow of hot nitrogen or hot argon. It also includes electrical resistance heating (flow of the electrical current through the substrate and heating it due to electrical resistance). Alternatively, the substrate is heated by direct contact with the support or other parts of the CVD equipment. By indirect heating is meant that the substrate is heated without direct contact between a heating source and the substrate. Preferred indirect ("non-contact") heating methods include heating of the substrate induced by electromagnetic induction, or by irradiation with microwave or IR radiation or by laser heating. Also, focused (localized) heating of specific location(s) can be applied instead of heating the whole substrate, by any of the above-mentioned means, if different multi-zone metallic coatings are desired at different positions of the substrate.

During steps a), c) and d) of the process according to the present invention, *i.e.* the steps wherein the coating is formed by means of MOCVD, the substrate is preferably surrounded by a suitable transport medium comprising a metal-containing precursor. Preferred transport media include a substantially saturated vapour, a substantially saturated vapour containing liquid droplets, or an unsaturated vapour. Besides the precursors, the transport medium may include delivery vehicles for the precursor such as inert gases, solvents, etc., as well as decomposition products such as saturated or unsaturated hydrocarbons, hydrogen, and other volatile compounds. The transport medium can comprise a volatile solvent such as hexane or heptane, since such solvents can improve the vapour saturation. In an embodiment of the invention that was found to be

efficient, the vapour consists of the precursor in the gaseous state, gaseous decomposition products of the precursor, which decomposition products are optionally recycled from earlier coating steps, and optionally one or more inert gases, like nitrogen, which inert gases are also optionally recycled from earlier coating steps.

The total deposition time in step a) and one or more steps c) is preferably at least 10 seconds, more preferably at least 30 seconds, even more preferably at least 1 minute, and most preferably at least 5 minutes. In one embodiment the deposition time is not longer than 3 hours, preferably 2 hours, more preferably 1 hour, and most preferably 30 minutes.

The total deposited layer obtained in steps a), c), and d) typically has a thickness of between 0.1 and 50 microns, and preferably between 3 and 30 microns.

The deposition steps of the process according to the present invention are preferably carried out at a pressure of at least 0.5 bara, more preferably of at least 0.8 bara. Preferably, the pressure is not higher than 2.0 bara, more preferably not higher than 1.2 bara. Most preferably, this step is performed at atmospheric pressure (about 1 bara).

The present invention furthermore relates to a substrate, preferably a metallic substrate, with a metallic coating obtainable by the above-disclosed process. Such coated substrate was found to have a reduced number of surface defects when compared to substrate coated in conventional MOCVD processes. More specifically, the coated substrate of the invention was found to be essentially free of surface defects, meaning that the coated substrate has less than 150, preferably less than 100, more preferably less than 50 surface defects, as defined above, per square cm.Typically the layer thickness is increased at the location of a defect.

The present invention furthermore relates to the use of the substrate having few surface defects in assemblies that are in contact with media such as chlorine, seawater, biodiesel, alcohol, fuel, cooling fluids, etc.; in assemblies that need to be painted and/or lacquered; in assemblies that are exposed to contact corrosion; in assemblies that need to be welded; in assemblies that are exposed to friction or wearing; in assemblies that have to have resistance against sticking and parts of which have dimensional tolerances of less than 50 micrometers (microns). Due to the smooth surface of the coated substrate, this will result in less off-specification product resulting from said use, thereby improving yields and reducing costs.

In an embodiment of the invention, the process contains additional steps, including one or more cleaning steps, one or more steps wherein the CVD equipment is flushed with an inert gas, one or more optional recovery steps for the metal-organic compound and/or its decomposition products, which, if applicable, can be recycled to the process, one or more polishing steps, one or more sintering steps, one or more heat treatments, one or more anodizing steps, one or more passivation steps, one or more oxidizing steps, one or more steps wherein a metal substrate is hardened, one or more coating steps wherein the parts are coated with one or more oils or conventional non-metallic coating layers, optionally containing colorants and/or pigments.

The present invention is elucidated by means of the following non-limiting examples. In all examples the equipment was kept at atmospheric pressure.
In these examples steel-alloy rivets with a diameter of 5 mm were coated with aluminium by contacting them, while hot, with vapours of triethyl aluminium (TEAL).
All rivets were pretreated by washing to remove grease and other foreign materials and subjected to a pickling step with HCl, after which they were dried by 3 acetone washes, and the rivets were stored under heptane until use.

The rivets were put in the CVD chamber and a nitrogen purge was used to evaporate heptane residue, and to ensure an oxygen and water-free atmosphere while the rivets were heated up. Pressure build-up was prevented by controlled venting. The coating chamber of about 60 litres was equipped with a bottom plate (support) which can be vibrated, an inlet tube for N_2 situated at the bottom and flowing through a perforated bottom plate with 120 holes of 2 mm in size, an induction coil for heating the metal substrate, and a source for alkyl vapours that can be combined with the N_2. The chamber wall and the induction coil were heated with oil to 200 and 170°C, respectively. The TEAL vapour was formed at a temperature of 240°C, using electrical heating.

Before actual coating takes place, batchwise, the rivets (substrates) are introduced into the coating chamber, heated up to the set point (see tables), which is done as fast as possible, while being put in motion by vibrating the bottom plate, after which the temperature of the rivets is maintained for the indicated period of time while about 10 g/min of metal alkyl is dosed into an evaporator (source of vapour) from the bottom, through the perforated plate, for a period as presented in the tables. The rivets were stationary or put in motion as specified in the tables. The temperature of the parts was measured using thermocouples and the induction heater was used to control the temperature of the rivets. During the whole process a 7 ml/min flow of nitrogen through the equipment was maintained.

Example 1 and Comparative examples A and B

In these examples rivets were used with a diameter of 5 mm and a length of 5 mm. A total of about 1,500 g of rivets (about 2,000 pieces/substrates) were coated per example. The metal alkyl precursor was continuously dosed in these examples.

Conditions:

	Ex.1	Ex.A	Ex.B
Dosing time of TEAL (minutes)	30	10	20
Total amount of TEAL dosed (g)	335	80	270
Substrate temperature (°C)	340	380	340
Vibration of bottom plate	periods of 5 s per minute	continuous	continuous
Heating	not during vibration	continuous	continuous

Results:

	Ex.1	Ex.A	Ex.B
Average Al layer thickness on rivet* (µm)	9.0	3.5	11.5
Surface defects **	3	7	7
Average surface defects size (mm^2)***	0.04	0.08	0.07
Averaged difference in layer thickness of defect***	100%	250%	200%
Number of defects per cm^{2***}	150	200	200

* = the Al layer thickness was calculated by measuring the weight of the Al on the surface (by dissolution of the Al from a number of rivets using NaOH), with knowledge of the surface area of the rivet and using an Al density of 2,700 kg/m^3.

** = judged on a visual scale, where 9 is bad (many surface defects) and 1 is excellent

*** = on smooth surfaces, particularly near the edges of the rivets, determined by light microscopy at a magnification of 200x

In Example 2, the above procedure of Example 1 was repeated, except that the coating conditions were changed.

Conditions were now such that after heating the substrates to 330°C with vibration, the vibration was stopped and the TEAL-vapour was introduced into the coating chamber for 5 minutes. Then, a process cycle started in which the induction heating was switched off and the rivets were allowed to cool to 220°C. After vibrating for 1 minute, causing the desired movement of the substrate, the heating was resumed and when the substrates reached a temperature of 330°C, they were kept at this temperature and TEAL was dosed again for 5 minutes. This cycle was repeated another 4 times.

In Example 3 the procedure of Example 2 was used, except that the process cycle was changed and about 1,500 g of rivets with a diameter of 3 mm and a length of 4 mm were coated. The change in the process cycle was that the rivets were allowed to cool to 260°C and that during the cooling down, TEAL-vapour was dosed at a rate of 2.5 g/min. Upon reaching this temperature, TEAL dosing was stopped. After vibrating for 1 minute, causing the desired movement of the substrate, the heating was resumed and TEAL was dosed at a rate of about 10g/min. When the substrates reached a temperature of 330°C, they were kept at this temperature and TEAL continued to be dosed for 5 more minutes.

After the last coating cycle of Examples 2 and 3, the rivets were cooled to 260°C without TEAL being dosed, vibrated for 1 minute, cooled further and rinsed three times with heptane (400 g per rinse).

Results:

	Ex.2	Ex.3
Average Al layer thickness on rivet* (µm)	4.6	11.1
Surface defects **	1	2
Average surface defects size (mm^2)***	<0.02	0.02
Averaged difference in layer thickness of defect***	20%	100%
Number of defects per cm^{2***}	40	100

* = the Al layer thickness was calculated by measuring the weight of the Al on the surface (by dissolution of the Al from a number of rivets using NaOH), with knowledge of the surface area of the rivet and using an Al density of 2,700 kg/m^3.

** = judged on a visual scale, where 9 is bad (many surface defects) and 1 is excellent

*** = on smooth surfaces, particularly near the edges of the rivets, determined by light microscopy at a magnification of 200x

Claims

1. Metal-Organic Chemical Vapour Deposition process wherein one or more substrates are supported in a CVD apparatus and wherein said process comprises two or more coating steps wherein the one or more substrates are brought into contact with a vapour of a metal-organic chemical and the conditions are controlled such that said metal-organic chemical decomposes and metal is deposited onto the substrate, and where said substrates are essentially not in motion in relation to one another and/or the support, and one or more movement steps wherein the one or more substrates are in motion in relation to one another and/or the support.

2. Metal-Organic Chemical Vapour Deposition process of claim 1 wherein essentially no metal is being deposited in the one or more movement steps.

3. Process according to claim 1 or 2 wherein the coating process is conducted in less than 180 minutes.

4. Process according to claim 1, 2, or 3 wherein multiple substrates are coated, with at least a step a) wherein the multiple substrates are essentially not in motion and contacted with said metal-organic compound-containing chemical vapour, with the metal-organic compound in said vapour being decomposed on the substrate's surface in order to deposit the metal of said metal-organic compound onto the substrate, a step b) wherein the substrates are put in motion with essentially no metal being deposited, and a step c) wherein the multiple substrates are essentially not in motion and again are subjected to a metal-organic compound-containing chemical vapour, with the metal-organic compound in said vapour being decomposed in order to deposit the metal of said metal-organic compound onto the substrate.

5. Process according to claim 4 wherein steps b) and c) are repeated at least once and step a) is optional.

6. Process according to either of claims 4 and 5 wherein the metal of the metal-organic compound in the metal-organic compound-containing chemical vapour is deposited onto the substrate in the deposition steps by thermal decomposition of the metal-organic compound.

7. Process according to any one of claims 4 – 6 wherein the temperature in one or more of the deposition steps is varied in order to control the diffusion of the deposited metal into the substrate, allowing the formation of a multi-zone coating.

8. Process according to any one of claims 4 – 7 wherein the total deposition time in the deposition steps is preferably at least 10 seconds, with the total deposition time being not longer than 2 hours.

9. Process according to any one of the preceding claims wherein the total amount of metal deposited forms a layer with a thickness of between 1 and 50 micrometers.

10. Process according to any one of the preceding claims wherein the metal-containing precursor is selected from the group consisting of aluminium alkyls, magnesium alkyls, zinc alkyls, aluminium alkylamides, magnesium alkylamides, zinc alkylamides, and volatile aluminium, magnesium or zinc organometallics comprising one or more cyclopentadienyl ligands.

11. Process according to any one of the preceding claims wherein the substrate according to the present invention is a metallic material selected from the group consisting of unalloyed steel, low alloyed steel, high alloyed steel, iron, cast iron, copper, a copper alloy, nickel, a nickel alloy, titanium, a

titanium alloy, alpha-titanium, beta-titanium, alpha-beta-titanium, gamma-titanium-aluminium, aluminium, cast aluminium, an aluminium alloy, magnesium, cast magnesium, a magnesium alloy, cobalt, a cobalt alloy, zinc, cast zinc, a zinc alloy, tin, and chromium.

12. Process according to any one of the preceding claims wherein the substrate is a metallized material, the metal of the metallic layer preferably being selected from the group consisting of zinc, a zinc-nickel alloy, a zinc-iron alloy, a zinc-tin alloy, a zinc-chromium alloy, a zinc-magnesium alloy, a zinc-aluminium alloy, a zinc-aluminium-magnesium alloy, and magnesium, or wherein the substrate has a layer of Galfan® or Galvalume®, where the metal layer does not have the same composition as the substrate, and where the metallic layer preferably has a thickness of 0.1 µm up to 1,000 µm.

13. Process according to any one of the preceding claims wherein the process contains any combination of additional steps, including one or more cleaning steps, one or more steps wherein the CVD equipment is flushed with an inert gas, one or more optional recovery steps for the metal-organic compound, which, if applicable, can be recycled to the process, one or more steps wherein the substrate is both in motion and being coated, one or more polishing steps, one or more sintering steps, one or more heat treatments, one or more anodizing steps, one or more passivation steps, one or more oxidizing steps, one or more steps wherein a metal substrate is hardened, one or more coating steps wherein the parts are coated with an oil or a conventional organic coating layer, optionally containing colorants and/or pigments.

14. A substrate obtainable by a process of any one of the previous claims having less than 150 surface defects per square cm.

15. Use of the coated substrate of the previous claim in assemblies that are in contact with media such as chlorine, demineralised water, seawater, biodiesel, alcohol, fuel, cooling fluids, etc.; in assemblies that need to be painted and/or lacquered; in assemblies exposed to contact corrosion; in assemblies that need to be welded; in assemblies exposed to friction or wearing, in assemblies that have to have resistance against sticking and parts of which have dimensional tolerances of less than 50 micrometers (microns).

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/059418

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C16/20 C23C16/46 C23C30/00
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)
C23C

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, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/012636 A1 (AKZO NOBEL CHEMICALS INTERNAT B V [NL]; BOROVIK ALEXANDER SERGEEVICH [) 3 February 2011 (2011-02-03) cited in the application page 5, line 11 - page 13, line 17; claims 1-12; examples 1-3,A,B	1-15
A	US 5 782 979 A (KANENO NOBUAKI [JP] ET AL) 21 July 1998 (1998-07-21) column 10, line 11 - column 11, line 8; figures 14(a)-(d)	1-15
A	US 2005/172895 A1 (KIJIMA TAKESHI [JP] ET AL) 11 August 2005 (2005-08-11) paragraph [0011] - paragraph [0015] paragraphs [0030], [0033]	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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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
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/059418

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		CN 102471882 A	23-05-2012
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