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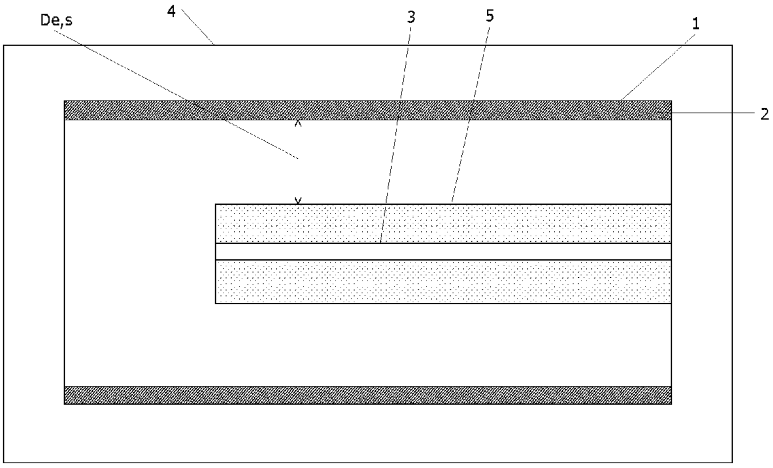

FIG 3.

(57) Abstract: The current invention relates to a method for PVD coating an internal surface of a hollow object, wherein the internal surface of the hollow object defines an internal volume, the method comprising the steps of: providing a cylindrical electrode having a radial outer surface, said cylindrical electrode comprising a target material, wherein said radial outer surface comprises said target material, within the internal volume of the hollow object, preferably coaxially positioned for a uniform coating, wherein said cylindrical electrode and said internal surface of the hollow object are separated by an average distance $D_{e,s}$ of at least 0.5 mm and at most 20 mm; and generating an electric field between the cylindrical electrode and the internal surface of the hollow object, wherein a product of a working pressure and the average distance $D_{e,s}$ lies between 0.01 Torr.cm and 10 Torr.cm.

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UNIFORM COATING OF A HOLLOW OBJECT AND METHOD THEREFOR

FIELD OF THE INVENTION

The present invention relates to a method for PVD coating an internal surface of a hollow object, particularly a hollow tube, using a cylindrical electrode.

In a second aspect, the present invention also relates to a hollow object with an internal surface comprising a PVD coating.

BACKGROUND

Hollow objects, such as pipes, housings, and valves, are often exposed to extreme conditions including high temperatures, mechanical stress, and chemical exposure. To extend the lifetime of these objects and enhance their surface properties, coatings are commonly applied on their internal surfaces. However, coating the internal surfaces of hollow objects can be challenging due to factors such as accessibility, geometry.

Various techniques have been developed for coating surfaces with different materials. One commonly used method for coating components is Physical Vapor Deposition (PVD), which involves depositing thin films of materials onto various surfaces. PVD processes, such as sputtering, cathodic arc evaporation, thermal evaporation, or electron beam evaporation, are often carried out in vacuum chambers where substrates, or workpieces, are placed on a substrate holder and exposed to a coating source. However, applying PVD coatings to the internal surfaces of hollow objects can be difficult as these processes are line-of-sight-based and are not capable of depositing coatings inside deep cavities.

An example is known in WO2022261684A1 and describes an apparatus and method for coating or modifying the inner surface of a hollow article using a plasma source with an elongate shape. The plasma source includes a cathode and a thermionic electron emission source target, connected in an electrically conductive manner. The apparatus also has a masking element that partially covers the outer surface of the cathode and the target to prevent plasma formation in the masked area during operation. The target has a plasma formation area that is not covered by the masking element. The invention also relates to a target, arrangement of the apparatus, method, and hollow article.

US8110043B2 describes an apparatus and method for applying coatings to the interior surfaces of components, such as pipes or tubes, using a vacuum chamber and an evaporant source. The primary carrier gas streams deflect the evaporated vapor flux from an area distal from and external to the substrate into the interior cavity, coating at least a portion of the interior of the longitudinal section of the substrate. The method involves the use of an energetic beam and primary carrier gas streams to direct the vapor flux towards the interior surfaces for coating.

Despite the advancements in PVD techniques, none of the existing methods fully meet the requirements of the industry in terms of robustness, process temperature, versatility, coating properties, and workpiece dimensions. Additionally, health and environmental risks associated with some of the existing techniques may limit their suitability for certain applications.

The present invention aims to resolve at least some of the problems and disadvantages mentioned above. The aim of the invention is to provide a method which eliminates those disadvantages. The present invention targets at solving at least one of the aforementioned disadvantages.

SUMMARY OF THE INVENTION

The present invention and embodiments thereof serve to provide a solution to one or more of above-mentioned disadvantages. To this end, the present invention relates to a method for PVD coating an internal surface of a hollow object according to claim 1. Preferred embodiments of the method are shown in any of the claims 2 to 13.

The present invention introduces a method for uniformly coating the interior surface of hollow objects, specifically small diameter tubes, using PVD. This method offers distinct advantages over other coating techniques. One of the advantages of this method is the ability to achieve a uniform coating thickness across the entire internal surface of the hollow object. Through isotropic sputtering of the target material in a radially homogeneous manner, the coating is consistent in thickness and quality, ensuring reliable and consistent performance in various applications. In addition, this method allows for precise control of the coating thickness. By carefully selecting the working pressure and distance between the electrode and the internal surface, the coating thickness can be accurately controlled, making it ideal for applications where precise coating thickness is crucial.

Another significant advantage is that this method is particularly well-suited for coating small diameter tubes. Coating small diameter tubes using conventional methods can be challenging, but this method overcomes those limitations, making it highly advantageous for small diameter tubing applications.

Furthermore, this method is capable of coating long hollow objects. This makes it suitable for coating continuous lengths of tubing or other long hollow objects, allowing for efficient and continuous operation in various industrial applications. Moreover, the method offers versatility in material selection, as it allows for the use of a variety of target materials. This enables customization of coatings with specific characteristics, such as low friction, high hardness, and resistance to mechanical, thermal, and chemical stress, making it adaptable for various applications.

Additionally, the method can accommodate multiple sub-electrodes in the cylindrical electrode, allowing for the deposition of multilayer coatings. This capability provides further versatility in tailoring coatings with complex compositions or properties, expanding its potential applications.

Lastly, the method can be combined with additional pre-treatment steps to further enhance the properties of the coating. This flexibility allows for additional customization and optimization of the coating properties for specific applications, making it a versatile and adaptable coating method.

The method thus allows for the deposition of coatings with controlled thickness, excellent adhesion, and specific characteristics, such as low friction, high hardness, resistance to mechanical and thermal stress, and resistance to chemical stress.

In a second aspect, the present invention relates to a hollow object with an internal surface comprising a PVD coating according to claim 14. A preferred embodiment of the method is shown in claim 15.

Having a hollow object with an internal surface that is coated with a physical vapor deposition (PVD) coating can offer several significant advantages in various applications. One of the key benefits is the enhanced performance that PVD coatings provide. These coatings are known for their exceptional mechanical and physical properties, including high hardness, low friction coefficient, wear resistance, and corrosion resistance. When applied to the internal surface of a hollow object, PVD coatings can significantly improve its performance and durability. This is particularly beneficial in industries such as automotive, aerospace, and energy, where components often face harsh conditions such as high temperatures, abrasive wear, or chemical exposure. The PVD coating acts as a protective barrier, extending the lifespan of the component and ensuring its optimal performance.

The PVD coating can be precisely tailored to meet specific performance requirements, such as optimizing frictional properties or enhancing wear resistance, without altering the external dimensions or shape of the object. This allows for greater freedom in designing complex shapes or lightweight structures, which can be advantageous in industries where weight reduction and performance optimization are critical factors. The compatibility with different materials makes PVD-coated hollow objects versatile and adaptable for various applications in different industries. Additionally, the precise coating thickness achieved through the PVD coating process ensures consistent and uniform coating quality, resulting in reliable performance and functionality in various applications.

In a third aspect the present invention relates to a use according to claim 16. The use as described herein provides an advantageous effect in terms of improved gas permeation barrier, solvent-free anti-corrosion protection, surface energy modification, and erosion resistance in various applications.

FIGURES

The following description of the figures of specific embodiments of the invention is merely exemplary in nature and is not intended to limit the present teachings, their application or uses. Throughout the drawings, corresponding reference numerals indicate like or corresponding parts and features.

Figure 1 shows a schematic representation of a cross-sectional view of a hollow object with its internal surface visible, highlighting the coaxial positioning of a cylindrical electrode according to an embodiment of the invention.
Figure 2 shows a schematic representation of a longitudinal section of a reaction chamber with a hollow object to be coated, where the cylindrical electrode is positioned coaxially within the hollow object according to an embodiment of the present invention.
Figure 3 shows a schematic representation of a longitudinal section of a reaction chamber, a hollow object and a coaxially positioned cylindrical electrode with a single type of target material, wherein the cylindrical electrode is shorter than the hollow object according to an embodiment of the invention.

Figure 4 shows a schematic representation of a longitudinal section of a reaction chamber illustrating a cylindrical electrode with three sub-electrodes positioned coaxially with a hollow object according to an embodiment of the invention.

Figure 5 shows a schematic representation of a longitudinal section of a coated hollow object with multiple layers of different coating materials forming a multi-coating structure on its internal surface according to an embodiment of the invention.

Figure 6 shows an example of a longitudinal section of a coated hollow object surface according to an embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention concerns a method for PVD coating an internal surface of a hollow object, particularly a hollow tube, using a cylindrical electrode.

Unless otherwise defined, all terms used in disclosing the invention, including technical and scientific terms, have the meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. By means of further guidance, term definitions are included to better appreciate the teaching of the present invention.

"A", "an", and "the" as used herein refers to both singular and plural referents unless the context clearly dictates otherwise. By way of example, "a compartment" refers to one or more than one compartment.

"About" as used herein referring to a measurable value such as a parameter, an amount, a temporal duration, and the like, is meant to encompass variations of +/-20% or less, preferably +/-10% or less, more preferably +/-5% or less, even more preferably +/-1% or less, and still more preferably +/-0.1% or less of and from the specified value, in so far such variations are appropriate to perform in the disclosed invention. However, it is to be understood that the value to which the modifier "about" refers is itself also specifically disclosed.

"Comprise", "comprising", and "comprises" and "comprised of" as used herein are synonymous with "include", "including", "includes" or "contain", "containing", "contains" and are inclusive or open-ended terms that specifies the presence of what follows e.g., component and do not exclude or preclude the presence of additional, non-recited components, features, element, members, steps, known in the art or disclosed therein.

Furthermore, the terms first, second, third and the like in the description and in the claims, are used for distinguishing between similar elements and not necessarily for describing a sequential or chronological order, unless specified. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other sequences than described or illustrated herein.

The recitation of numerical ranges by endpoints includes all numbers and fractions subsumed within that range, as well as the recited endpoints.

The expression "% by weight", "weight percent", "%wt" or "wt%", here and throughout the description unless otherwise defined, refers to the relative weight of the respective component based on the overall weight of the formulation.

Whereas the terms "one or more" or "at least one", such as one or more or at least one member(s) of a group of members, is clear *per se*, by means of further exemplification, the term encompasses *inter alia* a reference to any one of said members, or to any two or more of said members, such as, *e.g.,* any ≥3, ≥4, ≥5, ≥6 or ≥7 etc. of said members, and up to all said members.

Unless otherwise defined, all terms used in disclosing the invention, including technical and scientific terms, have the meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. By means of further guidance, definitions for the terms used in the description are included to better appreciate the teaching of the present invention. The terms or definitions used herein are provided solely to aid in the understanding of the invention.

Reference throughout this specification to "one embodiment" or "an embodiment" means that a particular feature, structure or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily all referring to the same embodiment, but may. Furthermore, the particular features, structures or characteristics may be combined in any suitable manner, as would be apparent to a person skilled in the art from this disclosure, in one or more embodiments. Furthermore, while some embodiments described herein include some but not other features included in other embodiments, combinations of features of different embodiments are meant to be within the scope of the invention, and form different embodiments, as would be understood by those in the art. For example, in the following claims, any of the claimed embodiments can be used in any combination.

In a first aspect, the invention provides a method for PVD coating an internal surface of a hollow object, wherein the internal surface of the hollow object defines an internal volume.

According to the invention, the term "hollow object", refers to any object that comprises an inner surface. Non-limiting examples of hollow objects are tubes, pipes, hollow shafts, or the like.

According to the invention, the term "inner surface", refers to a surface of an opening that extends into the hollow object. Non-limiting examples for internal surfaces are inner surfaces of boreholes, or those surfaces extending along the inner diameter surfaces of pipes, tubes, hollow shafts, or the like.

According to the invention, the term "PVD", refers to a process used to deposit thin films of material onto a surface. In a PVD process, a material is first evaporated from a solid source, typically using a high-energy source. This creates a vapor of the material, which then condenses onto a substrate, forming a thin film. The process takes place in a vacuum chamber, which is important because the absence of air and other gases prevents contamination of the film and ensures that the material can be deposited uniformly. In this context, the type of PVD technique is called sputtering. In sputtering, atoms are ejected from a target material by bombarding it with high-energy ions or plasma. The ejected atoms then condense on the substrate and form a thin film coating.

In a preferred embodiment of the invention, the method comprises providing a cylindrical electrode having a radial outer surface, said cylindrical electrode comprising a target material, wherein said radial outer surface comprises said target material, within the internal volume of the hollow object. This allows for isotropic sputtering, meaning that the target material is sputtered in a radially homogeneous way so that all areas of the internal surface are covered with the target material. This leads to a more uniform and consistent coating thickness on the internal surface of the hollow object. In a further preferred embodiment of the invention, is the cylindrical electrode coaxially positioned for a uniform coating. In this context, "coaxially positioned" means that the cylindrical electrode is placed in the centre of the hollow object to be coated, such that the longitudinal axis of the electrode is aligned with the longitudinal axis of the object. This ensures that the coating is deposited uniformly and evenly on the entire inner surface of the hollow piece. In other words, the distance between the internal surface and the cylindrical electrode is substantially homogeneous at every position. The coaxial positioning of the cylindrical electrode ensures that the distance between the internal surface of the hollow object and the electrode is substantially homogeneous at every position. This means that the coating is deposited consistently at the same distance from the internal surface throughout the entire interior of the hollow object, resulting in a uniform and consistent coating thickness.

In a preferred embodiment, the coating process utilizes a sputtering system that operates without the use of magnets, thereby eliminating any magnetic field influence. This non-magnetic sputtering approach is chosen to ensure a more straightforward and stable coating process. By avoiding the use of magnets, the system relies solely on the electric field to generate and sustain the plasma required for sputtering. This method is distinct from arc evaporation techniques, which often involve the use of magnetic fields to control the plasma and can lead to issues such as arc instability and droplet formation. The absence of magnetic fields in this sputtering process simplifies the setup and reduces the complexity of maintaining plasma stability. This approach enhances the uniformity and consistency of the coating, as it avoids the localized variations in plasma density that can occur with magnetically confined systems. The non-magnetic sputtering system is particularly advantageous for achieving high-quality, uniform coatings on the internal surfaces of hollow objects, ensuring reliable and reproducible results across various industrial applications.

In an even more preferred embodiment, the method is conducted using diode sputtering. Diode sputtering is a form of sputtering that operates without the use of magnets, relying solely on an applied electric field to create and sustain the plasma. This technique naturally achieves isotropic sputtering effects because it avoids the confinement associated with magnetic fields, ensuring a uniform coating distribution.

In a further preferred embodiment, the cylindrical electrode and the internal surface of the hollow object are separated by an average distance $D_{e,s}$ of at least 0.5 mm, more preferably at least 1.5 mm, more preferably at least 2.0 mm, more preferably at least 2.5 mm, more preferably at least 3.0 mm, more preferably at least 3.5 mm, more preferably at least 4.0 mm, more preferably at least 4.5 mm, more preferably at least 5 mm, more preferably at least 5.5 mm, more preferably at least 6.0 mm, more preferably at least 6.5 mm, more preferably at least 7.0 mm, more preferably at least 7.5 mm, more preferably at least 8.0 mm, more preferably at least 8.5 mm, more preferably at least 9.0 mm, more preferably at least 10.0 mm.

In a further preferred embodiment, the cylindrical electrode and the internal surface of the hollow object are separated by an average distance $D_{e,s}$ of at most 25.0 mm, more preferably at most 20.0 mm, more preferably at most 19.5 mm, more preferably at most 19.0 mm, more preferably at most 18.5 mm, more preferably at most 18.0 mm, more preferably at most 17.5 mm, more preferably at most 17.0 mm, more preferably at most 16.5 mm, more preferably at most 16.0 mm, more preferably at most 15.5 mm, more preferably at most 15.0 mm. more preferably at most 14.5 mm, more preferably at most 14.0 mm, more preferably at most 13.5 mm, more preferably at most 13.0 mm, more preferably at most 12.5 mm, more preferably at most 12.0 mm, more preferably at most 11.5 mm, more preferably at most 11.0 mm, more preferably at most 10.5 mm.

In a preferred embodiment, the cylindrical electrode and the internal surface of the hollow object are separated by an average distance $D_{e,s}$ of at most 10.0 mm, more preferably at most 9.5 mm, more preferably at most 9.0 mm, more preferably at most 8.5 mm, more preferably at most 8.0 mm, more preferably at most 7.5 mm, more preferably at most 7.0 mm, more preferably at most 6.5 mm, more preferably at most 6.0 mm, more preferably at most 5.5 mm, more preferably at most 5.0 mm, more preferably at most 4.5 mm, more preferably at most 4.0 mm, more preferably at most 3.5 mm, more preferably at most 3.0 mm, more preferably at most 2.5 mm, more preferably at most 2.0 mm.

In a further or an alternative embodiment, the cylindrical electrode and the internal surface of the hollow object are separated by an average distance $D_{e,s}$ of at least 0.5 mm and at most 5.0 mm, preferably at least 0.5 mm and at most 4.0 mm, more preferably at least 1.0 mm and at most 3.0 mm. This specific distance range is chosen to optimize the uniformity and quality of the coating process. Maintaining $D_{e,s}$ within this ideal range ensures that the electric field is evenly distributed across the internal surface, promoting consistent sputtering of the target material from the cathode. This leads to a uniform deposition of the coating material, enhancing the adhesion and overall quality of the coating. The controlled separation also minimizes the risk of uneven coating thickness and improves the efficiency of the deposition process.

According to the invention, the term “average distance”, denoted as $D_{e,s}$, represents the typical gap between the cylindrical electrode and the internal surface of the hollow object. It is important to note that the term "average distance" implies that there may be slight variations or fluctuations in the actual separation or gap between the electrode and the internal surface, but the mean or typical value should fall within the specified range.

The distance between the cylindrical electrode and the internal surface of the hollow object can be precisely controlled, which enables fine-tuning of the coating process parameters such as deposition rate, voltage, and current, leading to improved coating quality and reproducibility. By placing the cylindrical electrode in the center of the hollow object, the maximal distance possible between the internal surface and the cylindrical electrode can be achieved, without the cylindrical electrode coming into contact with the internal surface. This allows for an efficient and effective coating process, as the coating can be deposited evenly across the entire inner surface of the hollow object without any areas being missed. Such positioning of the cylindrical electrode ensures that the coating is deposited uniformly and evenly on the entire inner surface of the hollow object. This helps to achieve a consistent thickness of the deposited coating throughout the interior of the hollow object, resulting in a uniform and high-quality coating. The uniform coating achieved through such positioning of the cylindrical electrode helps to improve the overall quality of the coating. It minimizes the risk of uneven coating thickness, uneven coverage, or missed spots, which can result in poor coating quality and reduced performance of the coated object. It will further be understood that the maximal distance possible depends on the internal diameter of the hollow object.

In a preferred embodiment of the invention, the shape of the cylindrical electrode can be adapted to the diameter and size of the inner surface of the hollow object to be treated. For insertion into the hollow object, the outer diameter of the cylindrical electrode needs to be smaller than the inner diameter of the hollow object to be treated. The length of the cylindrical electrode may be as long as is needed for the inner surface to be treated completely.

In a preferred embodiment of the invention, the cylindrical electrode and hollow object are configured to move relative to one another, to allow for the coating of tubes or continuous operation, wherein the movement is parallel to maintain the coaxial positioning of the cylindrical electrode within the internal volume of the hollow object.

In a preferred embodiment of the invention, the target material forms a continuous and uniform radial outer surface of the cylindrical electrode. This means that the cylindrical electrode used for coating has a continuous and uniform radial outer surface that is made of the same material as the target material. In other words, the entire outer surface of the cylindrical electrode is made up of the same material that is intended to be deposited onto the surface of the hollow object being coated. This helps to ensure that the coating material is evenly and uniformly deposited onto the surface of the object, resulting in a high-quality coating.

In a preferred embodiment of the invention, the cylindrical electrode comprises a plurality of sub-electrodes arranged in series for achieving a multilayer coating, wherein each sub-electrode comprises the target material. The target material of at least two of the plurality of sub-electrodes can be the same or can be different. The sub-electrodes can be sequentially activated and deactivated to deposit different layers of material onto the internal surface of the hollow piece.

In a preferred embodiment of the invention, the target material of the cylindrical electrode and/or the sub-electrodes are selected from a group comprising a metal, a metal alloy, a ceramic material and combinations thereof. Alternatively or additionally, the metal is chromium. Alternatively or additionally, the target material comprises a ceramic material. More preferably, the target may comprise one or more materials/elements is selected from a group comprising: aluminum, boron, carbon, chromium, cobalt, copper, gold, holmium, iron, lanthanum, lithium, magnesium, manganese, molybdenum, nickel, silicon, silver, tin, titanium, vanadium, ytterbium, yttrium, zinc, zirconium, hafnium, tantalum, alloys thereof. These target materials allow for customization of the coating properties based on the specific requirements of the hollow object being coated. The specified target materials are known for their desirable properties, such as high thermal and electrical conductivity, excellent corrosion resistance, good mechanical strength, and other functional characteristics. Coating the internal surface of the hollow object with these materials can impart these properties to the coated object, enhancing its overall performance and durability. The coating process can be optimized for different applications, such as automotive, aerospace, electronics, energy, medical, and more.

In a further or alternative embodiment of the invention, the target material and/or the hollow object can be a magnetic or a non-magnetic material. In magnetron sputtering, magnets are used to trap electrons near the target surface, enhancing ionization and increasing the sputtering efficiency. This process is particularly beneficial for non-magnetic materials, which don’t interact with the magnetic fields of the magnets to maintain a dense plasma. These materials, such as aluminum, titanium, copper, gold, silver, zinc, platinum, tungsten, molybdenum, silicon, chromium, nickel, tantalum, ruthenium, and iridium. It should be mentioned that the use of magnetron sputtering with iron or Ni (magnetic materials) is difficult because the magnetic field of the substrates and /or targets interferes with the one of the magnets used for magnetron sputtering. Instead, non-magnetic PVD processes, such as diode sputtering, rely solely on electric fields to generate and sustain the plasma and magnetic or non-magnetic materials can be used for the target material and/or the hollow tube.

In a further of another embodiment, target materials are selected form the group of chromium (Cr), aluminum (Al), tungsten (W), tantalum (Ta), and titanium (Ti), as well as their carbides. These are optimal for applications aimed at preventing hydrogen permeation. These materials are particularly effective as hydrogen barriers due to their excellent resistance to hydrogen embrittlement and permeability. For instance, titanium and its carbides form dense coatings that effectively block hydrogen diffusion, making them ideal for components in hydrogen storage and transportation systems. Similarly, tungsten and tantalum offer superior mechanical strength and stability under high temperatures, providing robust protection in harsh environments.

In a further or another embodiment, target materials are selected form the group of platinum (Pt) and its alloys. These are optimal for applications requiring catalytic properties or enhanced corrosion protection. Platinum, known for its excellent catalytic activity, is widely used in catalytic converters and chemical reactors to promote various chemical reactions. Additionally, platinum coatings provide superior corrosion resistance, making them ideal for use in aggressive chemical environments. The inclusion of platinum alloys further enhances the coating's durability and performance, extending the lifespan of components exposed to corrosive substances.

In a further or another embodiment, target materials are selected form the group nickel (Ni), tantalum (Ta), carbon (C), and aluminum (Al). These are optimal in applications focused on corrosion protection. Nickel coatings are known for their excellent resistance to oxidation and corrosion, making them suitable for components exposed to harsh chemical and marine environments. Tantalum, with its high corrosion resistance and stability, is used in applications where long-term protection is critical. Carbon, in the form of diamond-like carbon (DLC), provides a hard, wear-resistant coating that also offers corrosion protection. Aluminum coatings, known for their lightweight and corrosion-resistant properties, are used in various industrial and automotive applications to protect against environmental degradation.

In a further of another embodiment, in non-reactive sputtering, the target materials are deposited as pure metals or alloys, resulting in metallic coatings with excellent electrical conductivity and reflectivity. In reactive sputtering, the target materials react with gases such as oxygen, nitrogen, or methane to form oxides, nitrides, or carbides, respectively. The versatility of the PVD process allows for both reactive and non-reactive sputtering of these target materials. This process enables the creation of coatings with tailored properties such as increased hardness, wear resistance, and chemical stability. For example, reactive sputtering of titanium in a nitrogen atmosphere forms titanium nitride (TiN), a hard, wear-resistant coating commonly used in cutting tools and decorative finishes. By carefully selecting target materials based on the specific application requirements, the PVD process can produce coatings with tailored properties that enhance the performance and durability of the coated components. The ability to use a wide range of target materials and sputtering techniques ensures that the PVD method is highly adaptable and versatile, meeting the diverse needs of various industrial applications.

In a preferred embodiment of the invention, the hollow object to be coated is provided, ie. Arrange or positioned or placed, in a reaction chamber. The hollow object can be provided in a vertical position with regards to the surface of the earth, in a horizontal position, or at an inclined position at an angle between 0° and 180° relative to the surface of the earth.

In a preferred embodiment of the invention, once the cylindrical electrode is arranged coaxially with the hollow object, the reaction chamber is closed and evacuated to reduce the working pressure within the chamber until a predetermined value is reached. This allows to remove any contaminants from the reaction chamber, such as moisture.

In a further preferred embodiment, a gas is passed through the reaction chamber. Consequently, the gas is provided in the internal volume of the hollow object comprising the cylindrical electrode. The working pressure is chosen so that the product of the working pressure and the average distance $D_{e,s}$ is between 0.01 Torr.cm and 10 Torr.cm, more preferably between 0.02 Torr.cm and 9 Torr.cm, more preferably between 0.03 Torr.cm and 8 Torr.cm, more preferably between 0.04 Torr.cm and 7 Torr.cm, more preferably between 0.05 Torr.cm and 6 Torr.cm, more preferably between 0.06 Torr.cm and 5 Torr.cm, more preferably between 0.07 more preferably between 0.08 Torr.cm and 4 Torr.cm, Torr.cm and 3 Torr.cm, more preferably between 0.09 Torr.cm and 2 Torr.cm, more preferably between 0.1 Torr.cm and 1 Torr.cm, more preferably between 10^{-5} Torr.cm and 45 Torr.cm, more preferably between 10^{-4} Torr.cm and 40 Torr.cm, more preferably between 10^{-3} Torr.cm and 35 Torr.cm, more preferably between 0.01 Torr.cm and 30 Torr.cm, more preferably between 0.1 Torr.cm and 25 Torr.cm, more preferably between 1 Torr.cm and 20 Torr.cm. This is one of the key parameters because it affects a lot the plasma characteristics and it is made possible only because the distance between the electrodes is small, due to the limited diameter of the hollow object to coat. The reason for specifying this range of working pressure is that it has been determined to be optimal for the coating process. Within this range, the electric field generated between the cylindrical electrode (cathode) and the internal surface of the hollow object (anode) is sufficient to facilitate the coating process and ensure uniform deposition of the coating material. The working pressure range is carefully selected to create a suitable environment for the coating process, allowing for efficient ionization of the target material, ion transport, and deposition on the internal surface of the hollow object. This range has been found to be effective in achieving the desired coating quality, thickness, and uniformity for the specific application of the invention. The specified working pressure range may also be influenced by other factors such as the properties of the target material, the type of coating process being used, the geometry and size of the hollow object, and other process parameters. Therefore, it is important to carefully control and maintain the working pressure within the specified range to optimize the coating process and achieve the desired coating results.

In a further or alternative embodiment, the working pressure is chosen so that the product of the working pressure and the average distance De,s is between 0.01 Torr.cm and 10 Torr.cm, preferably between 0.05 Torr.cm and 5 Torr.cm, more preferably between 0.1 Torr.cm and 5 Torr.cm, even more preferably between 0.1 Torr.cm and 4.5 Torr.cm, even more preferably between 0.1 Torr.cm and 4.5 Torr.cm, even more preferably between 0.1 Torr.cm and 3.5 Torr.cm, even more preferably between 0.1 Torr.cm and 3.0 Torr.cm, even more preferably between 0.1 torr.cm and 2.5 Torr.cm, even more preferably between 0.1 Torr.cm and 2.0 Torr.cm, and even more preferably between 0.1 Torr.cm and 1.5 Torr.cm.

In a further of alternative embodiment, the working pressure is between 0.01 Torr and 20 Torr, preferably between 0.1 Torr and 15 Torr, even more preferably between 1 Torr and 10 Torr, even more preferably between 1 Torr and 9 Torr, and even more preferably between 1 Torr and 8 Torr. In an embodiment, the working pressure is maintained between 0.01 Torr and 20 Torr, preferably between 0.1 Torr and 15 Torr, preferably between 1 Torr and 10 Torr, preferably between 1 Torr and 9 Torr, preferably between 1 Torr and 8 Torr, preferably between 0.01 Torr and 50 Torr, preferably between 0.1 Torr and 30 Torr, more preferably between 1 Torr and 20 Torr, even more preferably between 1 Torr and 15 Torr, and most preferably between 1 Torr and 10 Torr. Operating at these relatively higher pressures ensures optimal plasma generation and coating quality. Magnetron sputtering processes typically operate at lower pressures, in the range of milliTorr (mTorr), because the magnetic fields used in these processes trap electrons near the target surface. This trapping increases the probability of collisions with gas atoms, thereby enhancing ionization efficiency and allowing for higher plasma density at these lower pressures. In contrast, non-magnetic PVD processes, such as diode sputtering, rely solely on the electric field between the cathode and the anode to ionize the gas. Without the aid of magnetic confinement, maintaining a stable and efficient plasma requires higher pressures. At these higher pressures, the mean free path of electrons is shorter, which helps sustain ionization and maintain plasma stability. Therefore, specifying a higher working pressure inherently indicates that the method does not use magnetic fields. Effective plasma generation and maintenance at these pressures can only be achieved through electric fields alone, ensuring a stable and uniform coating process.

In a further of alternative embodiment, the cathode, represented by the cylindrical electrode, is positioned parallel to the anode, which is the internal surface of the hollow object. This parallel configuration ensures a uniform electric field distribution, which is critical for achieving a consistent and uniform coating. The cathode is fixed in place, meaning it does not move during the coating process. This fixed positioning of the cathode simplifies the setup and enhances the stability and reproducibility of the coating process. By maintaining a constant distance between the cathode and the anode, the method ensures that the isotropic sputtering effect remains consistent, leading to a uniform deposition of the target material on the internal surface of the hollow object. This configuration is particularly advantageous for coating long and small-diameter hollow objects, where precise control over the coating thickness and uniformity is essential.

In an alternative embodiment, the anode can be grounded to enhance the stability and control of the coating process. Grounding the anode ensures a stable electrical potential, minimizing electrical fluctuations and improving the uniformity of the coating. The process begins by cleaning and pre-treating the internal surface of the hollow object. The cylindrical electrode, acting as the cathode, is inserted into the hollow object, ensuring coaxial alignment and parallel positioning with the anode. The internal surface of the hollow object is then connected to the ground, either through a conductive wire or the chamber setup. Once the anode is grounded, the reaction chamber is evacuated to the desired pressure, removing residual gases. An inert or reactive gas is introduced, and an electric field is applied between the cathode and the grounded anode, maintaining a stable and uniform electric field. Plasma is ignited, and the target material is sputtered from the cathode and uniformly deposited onto the internal surface of the hollow object. Grounding the anode stabilizes the electric potential, reduces electrical disturbances, and ensures uniform deposition of the coating material. This configuration simplifies the setup and enhances the reliability and effectiveness of the PVD coating process, making it suitable for various industrial applications requiring precise and uniform coatings.

According to the invention, the term "working pressure", refers to the local, absolute pressure where the plasma is formed. The working pressure is measured near or at the target's surface. It thus represents the absolute pressure at or near the surface of the target where the plasma is formed. The working pressure relates to the equilibrium pressure that is achieved by simultaneously injecting gas and pumping in a plasma system. It is typically expressed as a product of pressure and distance, which provides a more accurate description of the type of plasma regime that is present. In cases where a gas mixture is injected, the working pressure is the sum of the pressures of the individual injected gases. When no gas is injected, the resulting pressure is referred to as the base pressure, which is significantly lower, approximately a million times, compared to the working pressure.

In a preferred embodiment of the invention, the gas provided in the internal volume may comprise a single gas or a mixture of two or more gases. Preferably, the gas comprises an inert gas, a reactive gas or a combination thereof. More preferably, the inert gas is selected from a group comprising helium, neon, argon, krypton. More preferably the reactive gas is selected from a group comprising nitrogen, oxygen, methane, ammonia, acetylene or fluorinated gases.

Preferably, the inert gas is argon. Argon is chosen for its excellent sputtering characteristics, as it efficiently ionizes and facilitates the sputtering of the target material without chemically reacting with it. This ensures a stable plasma environment conducive to consistent coating deposition.

Preferably, the reactive gas is selected from a group comprising nitrogen, oxygen, acetylene, or a combination thereof. The reactive gases—nitrogen, oxygen, and acetylene—are selected based on the desired properties of the final coating. Nitrogen is used to form nitrides, such as titanium nitride (TiN), which provide high hardness, wear resistance, and corrosion resistance. Oxygen is utilized to form oxides, like aluminium oxide (Al2O3) or titanium dioxide (TiO2), known for their excellent corrosion resistance and thermal stability. Acetylene is chosen for forming carbide coatings, such as titanium carbide (TiC), which offer superior hardness and wear resistance. By carefully selecting the reactive gas, the method can tailor the coating properties to meet specific industrial requirements, ensuring optimal performance and durability of the coated hollow objects.

Preferably, the gas comprises an inert gas and a reactive gas, wherein the inert gas is argon, and the reactive gas is selected from a group comprising nitrogen, oxygen, acetylene, or a combination thereof. Argon is utilized for its excellent sputtering characteristics, providing a stable and efficient plasma environment that facilitates the sputtering of the target material without undergoing chemical reactions itself. The addition of a reactive gas—nitrogen, oxygen, or acetylene—enables the formation of various compound coatings with tailored properties. By combining argon with one of these reactive gases, the method can produce high-quality coatings with specific desired properties, enhancing the performance and durability of the coated hollow objects for various industrial applications.

In a further preferred embodiment of the invention, the method further comprises generating an electric field between the cylindrical electrode and the internal surface of the hollow object, with the cylindrical electrode serving as a cathode and the hollow object serving as an anode. The electric field applied to the electrode is used to activate the gas into a plasma gas and to remove at least a portion of the target material from the cathode, which is then deposited on the internal surface of the hollow piece or tube.

When an electric field is applied to a cylindrical electrode, it activates or discharges the gas surrounding it, converting it into a plasma gas or a plasma discharge, i.e., the electric field ignites a plasma comprising the activated gas. This plasma gas, also referred to as the activated gas, is then used to remove at least a portion of the target material from the cathode particularly through the interaction of ions in the plasma gas with the cathode. The removed target material is then deposited onto the internal surface of the hollow object, known as the anode, resulting in the creation of treated hollow object. More specific, for the formation of a coating. This method of deposition is commonly known as sputtering. Therefore, the cylindrical electrode functions as a plasma source in this specific method. The use of a cylindrical electrode in this process leads to isotropic sputtering, where the target material is sputtered uniformly in a radially homogeneous manner, ensuring that all areas of the internal surface of the hollow object are evenly coated with the target material.

In a preferred embodiment of the invention, the gas discharge takes place in the Townsend regime. The Townsend regime is a concept in plasma physics that refers to a specific range of electric field strengths in which a plasma discharge occurs. In the Townsend regime, the electric field is strong enough to ionize the gas particles, creating a plasma, but not so strong as to cause significant electron multiplication through secondary electron emission. In the Townsend regime, the electric field strength is typically moderate, allowing for a stable and self-sustained plasma discharge. The behavior of the plasma in the Townsend regime is characterized by a linear relationship between the electric field and the ionization rate, known as the Townsend discharge law. This regime is commonly observed in many practical plasma applications, such as in gas discharges used in fluorescent lights, plasma displays, and certain types of plasma processing techniques. Understanding the Townsend regime is important for controlling and optimizing plasma processes in various technological applications. This results in a homogeneous discharge of a large radius, and contributes to the homogeneity and uniformity of the obtained coating.

In a preferred embodiment of the invention, the type of electric field applied to the cylindrical electrode for the plasma gas activation and sputtering process can vary. Both AC (alternating current) and DC (direct current) can potentially be used for this purpose, as long as the electric field is applied for a duration sufficiently long to form a layer of target material on the internal surface.

In some cases, DC power is commonly used for sputtering, where a constant voltage or current is applied to the electrode to generate the plasma gas and facilitate the removal and deposition of target material. DC sputtering is known for its simplicity and ease of control, making it a popular choice for many applications. On the other hand, AC power can also be used for sputtering, where the polarity of the electric field alternates periodically. AC sputtering includes techniques such as RF sputtering. These methods offer specific advantages in certain situations. AC sputtering is known to provide some advantages in certain situations, such as improved uniformity of the deposited coating and reduced arcing. The choice between AC and DC power for sputtering depends on various factors, including the specific material being deposited, the desired coating properties, and the equipment setup.

In a preferred embodiment of the invention, a power density applied to the cathode is preferably between 0.01 W/cm² and 50 W/cm², preferably between 0.01 W/cm² and 40 W/cm², preferably between 0.05 W/cm² and 30 W/cm², preferably between 0.1 W/cm² and 35 W/cm², preferably between 0.03 W/cm² and 25 W/cm², preferably between 0.01 W/cm² and 5 W/cm², preferably between 0.05 W/cm² and 2 W/cm², preferably between 0.1 W/cm² and 2 W/cm², preferably between 0.1 W/cm² and 8 W/cm², preferably between 0.1 W/cm² and 25 W/cm², preferably between 0.2 W/cm² and 5 W/cm², preferably between 0.5 W/cm² and 10 W/cm², preferably between 0.5 W/cm² and 15 W/cm², preferably between 1 W/cm² and 10 W/cm², preferably between 1 W/cm² and 20 W/cm², preferably between 0.05 W/cm² and 25 W/cm² , preferably between 0.2 W/cm² and 10 W/cm², preferably between 0.2 W/cm² and 15 W/cm², preferably between 0.01 W/cm² and 20 W/cm², preferably between 0.05 W/cm² and 10 W/cm². Power density refers to the amount of power applied per unit area of the cathode surface. The proposed densities can result in increased ion bombardment energy, which can affect the coating properties such as coating adhesion, microstructure, and thickness control. Higher power densities can also lead to higher deposition rates, which can impact the overall process efficiency and productivity.

In a further or alternative embodiment of the invention, a power density applied to the cathode is between 0.1 W/cm² and 50 W/cm², preferably between 0.1 W/cm² and 25 W/cm², preferably between 1.0 W/cm² and 20 W/cm², preferably between 1.0 W/cm² and 10 W/cm², preferably between 1.5 W/cm² and 10 W/cm², preferably between 2.0 W/cm² and 10 W/cm², preferably between 2.5 W/cm² and 9.0 W/cm², preferably between 3.0 W/cm² and 9.0 W/cm², preferably between 3.5 W/cm² and 8.5 W/cm², and even more preferably between 4.0 W/cm² and 8.0 W/cm². This specific range is even more ideal to optimize the sputtering process, ensuring efficient ionization of the gas and uniform deposition of the target material onto the internal surface of the hollow object. By maintaining the power density within this range, the coating process achieves a balance between deposition rate and coating quality, resulting in a uniform, high-quality coating with excellent adhesion and desired properties. This controlled power density range is particularly effective for achieving consistent results in various industrial applications requiring precise and uniform coatings.

In a preferred embodiment of the invention, an average current density applied to the cathode is preferably between 0.001 A/cm² and 10 A/cm², preferably between 0.002 A/cm² and 9 A/cm², preferably between 0.003 A/cm² and 8 A/cm², preferably between 0.004 A/cm² and 7 A/cm²,preferably between 0.005 A/cm² and 6 A/cm², preferably between 0.001 A/cm² and 0.5 A/cm², preferably between 0.001 A/cm² and 1 A/cm², preferably between 0.001 A/cm² and 5 A/cm², preferably between 0.001 A/cm² and 10 A/cm², preferably between 0.005 A/cm² and 0.5 A/cm², preferably between 0.005 A/cm² and 1 A/cm², preferably between 0.005 A/cm² and 5 A/cm², preferably between 0.01 A/cm² and 0.5 A/cm², preferably between 0.01 A/cm² and 1 A/cm², preferably between 0.01 A/cm² and 5 A/cm², preferably between 0.01 A/cm² and 10 A/cm². The average current density refers to the amount of electric current passing through the cathode per unit area. The average current density affects the ionization of the process gas and the generation of plasma, which in turn influences the ion bombardment energy and the resulting coating characteristics. For very thin films, low currents such as 0.001 A/cm² can be particularly useful. Higher average current densities can result in higher plasma densities and increased ion bombardment energy, which can affect the coating properties such as coating adhesion, density, and microstructure.

In a further or alternative embodiment of the invention, an average current density applied to the cathode is preferably between 0.001 A/cm² and 5 A/cm², preferably between 0.001 A/cm² and 2.5 A/cm², preferably between 0.001 A/cm² and 1 A/cm², preferably between 0.002 A/cm² and 1 A/cm²,preferably between 0.002 A/cm² and 0.1 A/cm², preferably between 0.002 A/cm² and 0.05 A/cm², preferably between 0.003 A/cm² and 0.05 A/cm², preferably between 0.003 A/cm² and 0.05 A/cm², preferably between 0.004 A/cm² and 0.05 A/cm², preferably between 0.004 A/cm² and 0.04 A/cm², and even more preferably between 0.004 A/cm² and 0.03 A/cm². This range provides even more benefits. It ensures efficient ionization of the gas, generating a stable plasma that facilitates the uniform deposition of the target material onto the internal surface of the hollow object. Maintaining the current density within this range helps to achieve a balance between deposition rate and coating quality, resulting in a uniform, high-quality coating with excellent adhesion and desired properties. It minimizes the risk of excessive heating or damage to the substrate, ensuring the integrity of both the coating and the underlying material. Additionally, it allows for more precise control over the deposition process, reducing variability and enhancing reproducibility. This controlled current density range is particularly effective for achieving consistent results in various industrial applications requiring precise and uniform coatings, thereby optimizing the overall performance and durability of the coated hollow objects.

Optimizing the power density and average current density within the preferred ranges can help achieve desired outcomes in the coating process. However, the specific effects of power density and average current density on the coating process would depend on various factors such as the material being processed, the electrode configuration, the process gas, and other process parameters. Therefore, careful consideration and adjustment of these parameters based on the specific coating requirements and process conditions are necessary to achieve the desired coating properties and performance.

In a further or another embodiment, an average voltages ranges from 50 V to 2 500 V, preferably from 100 V to 1 500 V, more preferably from 150 V to 1 000 V, even more preferably from 200 to 800 V. The target-substrate distance in the PVD coating process is kept very close, allowing for operation at low voltages. This proximity between the target and the substrate is a key factor in achieving high-quality coatings. Operating at these low voltages offers several advantages, including the ability to use a wide range of power supplies. Notably, High Power Impulse Magnetron Sputtering (HIPIMS) can be effectively employed under these conditions. HIPIMS is known for its ability to produce dense and smooth coatings with excellent adhesion properties. By maintaining a short distance between the target and the substrate, the mean free path of the sputtered atoms is reduced, leading to fewer collisions and higher energy upon impact with the substrate. This results in a coating with superior quality and uniformity. The use of low voltage in conjunction with the short target-substrate distance not only enhances the quality of the coating but also allows for more efficient energy use during the deposition process. The low-voltage operation minimizes the risk of substrate overheating and reduces energy consumption, making the process more cost-effective and environmentally friendly. The versatility of using various power supplies, including HIPIMS, under these conditions ensures that the method can be adapted for different materials and applications, providing high flexibility in the coating process. If high voltage were to be used, the short distance would likely result in the development of an arcing regime due to the high electric field strength between the electrodes. Arcing can lead to defects in the coating, such as micro-cracks and non-uniform deposition, which degrade the quality of the coated surface. By operating at lower voltages, the process avoids the onset of arcing, thereby maintaining the integrity and consistency of the coating. This approach ensures that the coated surface is free from defects and possesses the desired mechanical and chemical properties. The close proximity allows for a higher rate of material transfer from the target to the substrate, resulting in faster coating deposition. This is particularly advantageous for industrial applications where high throughput and quick turnaround times are essential. The method ensures that even with the increased deposition rate, the quality of the coating remains high, providing a robust and reliable solution for various coating applications.

In a further or alternative embodiment of the invention, a low voltage and low current is applied. More preferably an average current density ranges between 0.001 A/cm^2 and 10 A/cm^2, more preferably between 0.004 A/cm^2 and 0.03 A/cm^2, and the voltage ranges from 200 V to 800 V. In magnetron sputtering, magnets are used to confine the plasma near the target, allowing for higher plasma densities at lower voltages and higher currents. This magnetic confinement enhances ionization efficiency but requires a specific setup involving magnets. In contrast, diode sputtering does not use magnetic fields and instead relies on the applied electric field alone to achieve sufficient plasma density and ionization of the gas. The specified electrical parameters ensure efficient ionization of the gas and uniform deposition of the target material onto the internal surface of the hollow object without the need for magnetic fields. The low voltage provides sufficient energy to ionize the gas and create a stable plasma, while the low current maintains process efficiency and prevents excessive heating of the substrate. Consequently, the use of low voltage and low current within the specified ranges inherently supports a non-magnetic PVD process. This setup achieves the desired coating properties through the applied electric field alone, distinguishing it from magnetron sputtering techniques that require magnetic fields for plasma confinement. Therefore, the specified electrical characteristics clearly indicate a non-magnetic PVD method, ensuring efficient and uniform coating deposition.

In a preferred embodiment of the invention, the method comprises a step of pre-treating the internal surface of the hollow object prior to depositing the target material onto the internal surface, i.e., prior to coating the internal surface. Preferably, the pre-treatment is performed prior to placing the hollow object in the reaction chamber. Ideally, the pre-treatment is conducted in the same reaction chamber used for the coating deposition process, offering convenience and efficiency. For the pre-treatment, a plasma-assisted approach is preferred. This pre-treatment can be conducted exclusively or predominantly within the reaction chamber itself. The plasma-assisted pre-treatment occurs after achieving the predetermined working pressure value but before introducing the gas used to remove the target material from the electrode. This sequence ensures optimal timing for the pre-treatment step in relation to the overall process. It is important to note that the specifics of the pre-treatment can vary. The pre-treatment can be performed at the same pressure as the sputtering process or at a different pressure. Similarly, the pre-treatment can utilize the same gas as the sputtering process or a different gas. However, in the pre-treatment step, the polarity is reversed to ensure that it is the hollow object itself that undergoes the "sputtering" process, effectively cleaning and preparing its internal surface. In a preferred embodiment of the invention, the pre-treatment comprises a cleaning and/or an etching step, for example ultrasonic cleaning or sandblasting. According to the present disclosure, the term "cleaning" refers to the process of removing contaminants, particularly organic contaminants, from a surface. In other words, "cleaning" refers to the basic removal of contaminants. On the other hand, in the context of the present invention, "etching" refers to a process that involves both the removal of contaminants and the attachment of specific functional groups to the internal surface of a hollow object. These functional groups are intended to enhance the adhesion of a target material coating to the surface. In other words, "etching" encompasses a more comprehensive process that not only removes contaminants but also modifies the surface by adding functional groups that facilitate the bonding of a coating material.

In a further preferred embodiment of the invention, the pre-treatment comprises an etching step. Preferably, the plasma assisted etching is performed in the reaction chamber upon reaching the predetermined working pressure and prior to passing the gas through the reaction chamber. The plasma assisted etching comprises passing an etching gas through the reaction chamber, thereby providing the etching gas in the internal volume of the hollow object. Next, a second electric field is applied to the hollow object, with the cylindrical electrode serving as the anode and the hollow object serving as the cathode. The second electric field advantageously activates the etching gas, thereby obtaining an etching plasma. The ions of the etching plasma break down organic contaminants at the surface of the internal surface of the hollow object, resulting in volatile components which are removed by the etching gas. The ions of the etching plasma also attach to the internal surface, thereby providing the internal surface with functional groups.

In a further preferred embodiment of the invention, the etching gas is selected from a group comprising argon, helium, nitrogen, oxygen, methane, ethylene, nitrogen dioxide, nitrous oxide or fluor.

In a further of another embodiment of the invention, the pre-treatment processes employed may include solvent cleaning and/or sandblasting and/or plasma etching. Each method can be selected based on the specific requirements of the application, ensuring that the resulting coating adheres well and provides the desired performance characteristics. By combining these pre-treatment steps, the method ensures that the hollow object's internal surface is optimally prepared, leading to high-quality, uniform PVD coatings with excellent adhesion and durability.

In a further of another embodiment, the internal surface of the hollow object undergoes a solvent cleaning process to remove contaminants such as oils, grease, and other organic residues. The object is immersed in a solvent bath containing an appropriate cleaning solvent, such as acetone, ethanol, or isopropanol. Ultrasonic agitation is applied to the solvent bath to enhance the cleaning efficiency by breaking down and removing stubborn contaminants. Following this, the hollow object is thoroughly rinsed with fresh solvent to ensure all contaminants are removed. The cleaned object is then dried using a hot air blower or placed in a drying oven to evaporate any remaining solvent. This method effectively removes a wide range of organic contaminants and is relatively simple to implement in various industrial settings.

In a further of another embodiment, sandblasting is employed to clean and roughen the internal surface of the hollow object. This process not only removes contaminants but also creates a rough surface profile, enhancing the adhesion of the subsequent PVD coating. The hollow object is placed in a sandblasting chamber, where an abrasive material, such as aluminium oxide or silicon carbide, is blasted at high velocity onto the internal surface using compressed air. The sandblasting process effectively removes oxides, scale, and other surface contaminants, while also creating a textured surface that significantly improves coating adhesion. After sandblasting, the object is thoroughly cleaned with compressed air to remove any residual abrasive particles.

In a second aspect, the invention provides a hollow object with an internal surface comprising a PVD coating.

In a particularly preferred embodiment, the hollow object has an internal diameter smaller than 5 cm, the coating has a thickness between 0.01 µm and 50 µm, and a relative deviation of the thickness of the coating is at most 20%.

In a further or another embodiment, the thickness of the PVD coating applied to the internal surface of the hollow object can range from 100 nm to 20 000 nm, more preferably from 200 nm to 15 000 nm, even more preferably from 300 nm to 10 000 nm, even more preferably from 500 nm to 9 000 nm, even more preferably from 600 nm to 8 000 nm, even more preferably from 700 nm to 7 000 nm, even more preferably from 800 nm to 6 000 nm, even more preferably from 900 nm to 5 000 nm, even more preferably from 1 000 nm to 4 000 nm. Alternative the thickness of the coating is between 100 nm and 4 000 nm, between 200 nm and 20 000 nm, between 100 nm and 10 000nm, between 100 nm and 1 000 nm or between 500 nm and 10 000 nm, depending on the desired properties and intended use of the coated object. Precise control of the deposition rate is achieved through a meticulous calibration process. Initially, the system is calibrated under identified deposition conditions, including parameters such as power density, gas flow rates, and working pressure. This calibration involves performing a series of test runs to determine the optimal conditions that result in the desired deposition rate. By fine-tuning these parameters, the system can consistently produce coatings with the specified thickness, ensuring that the final product meets the application’s performance criteria.

In an embodiment, sacrificial parts are employed on either side of the tube during the PVD process to ensure the uniformity of the coating across the entire internal surface of the hollow object. These sacrificial parts play a crucial role in extending the plasma beyond the ends of the hollow object. By doing so, they help maintain a consistent plasma density and ion flux along the full length of the internal surface. The extended plasma region facilitated by the sacrificial parts ensures that the coating is uniformly applied, avoiding any edge effects or variations in thickness that could occur at the ends of the tube. This method guarantees that the coating has a homogeneous thickness throughout the entire internal surface, resulting in a high-quality, uniform coating. The use of sacrificial parts to extend the plasma is particularly advantageous in applications requiring precise and uniform coatings, as it ensures that the internal surface of the hollow object receives an even and consistent layer of the coating material. This approach enhances the reliability and performance of the coated object in its intended application, whether it be for improved wear resistance, corrosion protection, or other functional properties provided by the PVD coating. Through this embodiment, the invention demonstrates its capability to produce high-quality, uniform coatings on the internal surfaces of hollow objects, meeting the stringent requirements of various industrial applications.

In a preferred embodiment of the invention, a ratio of a length of the hollow object to its internal diameter is at least 10, preferably at least 15, more preferably at least 20, more preferably at least 25, more preferably at least 30, more preferably at least 40, more preferably at least 45, more preferably at least 50, more preferably at least 50, more preferably at least 60, more preferably at least 70, more preferably at least 80, more preferably at least 90, more preferably at least 100.

In a preferred embodiment of the invention, a ratio of a length of the hollow object to its internal diameter is at most 10000, more preferably at most 5000, more preferably at most 4500, more preferably at most 4000, more preferably at most 3500, more preferably at most 3000, more preferably at most 2500, more preferably at most 2000, more preferably at most 1500, more preferably at most 1000, more preferably at most 500, more preferably at most 400, more preferably at most 300, more preferably at most 200.

Most preferably, the ratio of the length of the hollow object to its internal diameter ranges between 10 and 2000, preferably between 15 and 1500, more preferably between 20 and 1000, more preferably between 25 and 500, more preferably between 30 and 400, more preferably between 40 and 300, more preferably between 50 and 200.

Preferably, the internal diameter of the hollow object is at least 0.1 mm, preferably at least 0.5 mm, more preferably at least 1.0 mm, more preferably at least 2.0 mm, more preferably at least 3.0 mm, more preferably at least 4.0 mm, more preferably at least 5.0 mm, more preferably at least 6.0 mm, more preferably at least 7.0 mm, more preferably at least 8.0 mm, more preferably at least 9.0 mm, more preferably at least 10.0 mm, more preferably at least 15.0 mm, more preferably at least 20.0 mm, more preferably at least 25.0 mm.

Preferably, the internal diameter of the hollow object is at most 50.0 mm, preferably at most 49.0 mm, more preferably at most 48.0 mm, more preferably at most 47.0 mm, more preferably at most 46.0 mm, more preferably at most 45.0 mm, more preferably at most 44.0 mm, more preferably at most 43.0 mm, more preferably at most 42.0 mm, more preferably at most 41.0 mm, more preferably at most 40.0 mm, more preferably at most 39.0 mm, more preferably at most 38.0 mm, more preferably at most 37.0 mm, more preferably at most 36.0 mm, more preferably at most 35.0 mm, more preferably at most 34.0 mm, more preferably at most 33.0 mm, more preferably at most 32.0 mm, more preferably at most 31.0 mm, more preferably at most 30.0 mm,.

In a further preferred embodiment of the invention, the hollow object has the form of a hollow tube or cylinder. In other words, the internal surface of the hollow object defines an internal volume. The hollow object is for example, made steel and steel-based alloys.

In an embodiment of the invention, the formed coating is a tribological coating. Tribological coatings are used in applications that are exposed to severe contact forces under which normal thin-film coatings would fracture and lose adherence, thereby forfeiting their protective function. These coatings are designed to have low friction coefficients, high hardness, and increased durability to resist wear caused by different forms such as adhesive welding, shearing, abrasion, high-speed particle impact, erosion, corrosion, and high temperature-induced chemical interaction. Examples of applications that benefit from tribological coatings include metal cutting tools, surfaces operating at high temperatures, optical surfaces exposed to high-velocity impact, and surfaces exposed to contact abrasion and corrosive liquids.

Tribological coatings find applications in a wide range of industries, including machining, medical implants, military air and sea vehicles, commercial decorative metals, and polymer surfaces. An example of tribological coatings in commercial use is the adaptation of military technology for supersonic aircraft, where coatings such as diamond-like carbon (DLC), germanium carbide (GeC), boron nitride (BN), and others are used to protect optical windows against erosion from sand, dust, and rain. These coatings also find use in thermal infrared (IR) imaging windows for high-end cars and environmental protection in military operations in harsh environments.

Multilayer coatings are often employed for tribological applications, as they offer enhanced performance compared to monolayer coatings. Typically, tribological coatings have a thickness ranging from 5 to 30 µm, and multilayer coatings consist of alternating layers of hard resistant materials and softer materials to reduce internal stresses and increase durability. Our method allows for the convenient development of multilayer coatings by simply switching the gas used. Examples of highly interesting material pairs for tribological coatings include Ti/TiC, Ti/TiN, TiAl/TiAlN, Cr/CrN, and Ta/TaN. Additionally, materials such as nitrides, carbides, and diamond-like carbon (DLC) are excellent candidates for tribological coatings due to their wear resistance properties, which cannot be achieved through electrodeposition methods.

In an embodiment of the invention, the coating formed is designed to allow gas permeation. Gas permeation is a multifaceted process involving absorption, dissociation, diffusion, recombination, and desorption of gas molecules, similar to the phenomenon of material outgassing. The coating is specifically engineered to facilitate the controlled movement of gas molecules through its structure, while maintaining its integrity and performance characteristics. This gas permeation capability of the coating makes it suitable for applications where controlled gas transport or barrier properties are desired, such as in gas separation, packaging, or other specialized environments. For gas permeation barriers, a dense coating is typically needed, which can be obtained through sputtering. The materials considered for gas permeation barriers are mainly nitrides, similar to tribological applications. However, the thickness of the coating is generally thinner, around 1 µm. Some of the most promising materials for hydrogen permeation barriers are TiN, TiAlN, SiN, and SiC. For other gases, oxides such as Al2O3 or SiO2 can also be included as coating materials.

In a further or another embodiment of the invention, some of the most promising materials for hydrogen permeation barriers include chromium (Cr), aluminium (Al), tungsten (W), tantalum (Ta), and titanium (Ti). Additionally, their respective alloys, as well as their carbides, nitrides, and oxides, are also considered effective for this application. This selection is made because these gases offer distinct advantages in the physical vapor deposition (PVD) process, enhancing the properties of the resulting coatings.

Nitrogen is commonly used in PVD processes to form nitrides, such as titanium nitride (TiN), which are known for their high hardness, wear resistance, and corrosion resistance. Nitrogen helps in creating coatings that are highly durable and suitable for applications requiring robust surface protection.

Oxygen is used to form oxides, such as aluminium oxide (Al_2O_3) or titanium dioxide (TiO2), which provide excellent corrosion resistance, high hardness, and thermal stability. Coatings formed with oxygen are ideal for applications exposed to harsh environments or high temperatures.

Acetylene is a hydrocarbon gas that is used to create carbide coatings, such as titanium carbide (TiC), which offer high hardness and excellent wear resistance. Carbide coatings are particularly beneficial for applications involving high mechanical stress or abrasive wear.

By selecting these specific reactive gases, the method can produce coatings with tailored properties that meet the demands of various industrial applications. Each gas contributes to the formation of coatings with unique characteristics, such as enhanced hardness, wear resistance, corrosion resistance, or thermal stability, making the coatings highly effective and versatile for a wide range of uses. Furthermore, the inclusion of alloys, as well as their carbides, nitrides, and oxides, is considered effective for this application because these materials provide enhanced and tailored properties that meet the specific demands of various industrial applications. Alloys offer superior mechanical properties, such as increased strength, toughness, and durability, making them ideal for robust and resilient coatings. Carbides, like titanium carbide (TiC), provide extremely high hardness and wear resistance, suitable for surfaces subjected to intense mechanical stress and abrasion. Nitrides, such as titanium nitride (TiN), offer excellent hardness, wear resistance, and corrosion resistance, crucial for extending the lifespan of components in harsh environments. Oxides, like aluminium oxide (Al2O3), are known for their high hardness, thermal stability, and excellent resistance to corrosion and wear, making them important for applications exposed to high temperatures and corrosive environments. The ability to form coatings with specific combinations of elements allows for fine-tuning the properties to suit particular applications, enhancing their versatility and adaptability. This results in improved performance characteristics, leading to longer-lasting coatings that maintain their protective qualities over extended periods, reducing the need for frequent maintenance or replacement. By considering these materials for the coating process, the method ensures optimal properties for a wide range of demanding applications.

In an embodiment of the invention, the coating formed is designed to provide corrosion resistance. This coating can be applied to pipes or other components that are in contact with corrosive fluids, providing a protective barrier to prevent corrosion and extend the lifespan of the material. The coating is typically composed of oxides or nitrides, with thicknesses ranging from 1 to 10 µm. Materials commonly used for corrosion-resistant coatings include SiO_2, Al_2O_3, ZrO_2, $ZrSiO_4$, TiN, and TiAlN. These materials are chosen for their excellent corrosion resistance properties, which can prevent or reduce the degradation of the underlying material due to chemical reactions with corrosive fluids. This corrosion-resistant coating can find applications in various industries where protection against corrosive environments is critical, such as oil and gas, chemical processing, marine, and automotive industries.

In an embodiment of the invention, the coating formed is designed to function as a catalyst. This coating can be applied to the tubes inside or after a chemical reactor, where it can promote or accelerate specific chemical reactions. The choice of catalyst material will depend on the desired reaction and operating conditions, but generally, metallic coatings, particularly noble metals such as Pt, Pd, Au, or their oxides, are commonly used for catalysis.

Unlike gas permeation or corrosion-resistant coatings, catalytic coatings are typically much thinner, often in the nanometer scale, to maximize the surface area available for catalytic activity. The coating is engineered to provide high catalytic activity and selectivity, while maintaining stability and durability under the operating conditions of the chemical reaction. The properties of the catalyst coating, such as its composition, morphology, and thickness, can be tailored based on the specific requirements of the targeted chemical reaction. Coating tubular objects with catalysts can significantly enhance the efficiency and performance of chemical processes in industries such as petrochemicals, pharmaceuticals, and environmental applications. The use of catalyst coatings can enable higher conversion rates, lower reaction temperatures, reduced energy consumption, and improved product selectivity, making them valuable for various catalytic applications in different industries.

In an embodiment of the invention, the coating formed is designed to be conductive. This conductive coating can be applied inside a tube, and it can serve various purposes depending on the specific application. For instance, copper (Cu) and silver (Ag) are commonly used as conductive coating materials when transparency is not a requirement. These coatings can enable electrical conductivity, making them suitable for applications where electrical current needs to flow through the coated surface, such as in electronic devices, sensors, or wiring. In some cases, transparency may be desired, such as in glass tubes or other transparent substrates. In such scenarios, Indium Tin Oxide (ITO) can be used as a coating material. ITO is a transparent conductive material that can be deposited as a thin coating, allowing light to pass through while maintaining its conductive properties. This makes it suitable for applications where both electrical conductivity and transparency are required, such as in touchscreens, displays, or optical sensors. The thickness and composition of the conductive coating can be optimized based on the specific requirements of the application, including factors such as electrical conductivity, transparency, adhesion, and durability. Conductive coatings can provide enhanced functionality and performance to a wide range of applications, making them valuable in various industries, including electronics, optics, automotive, and aerospace.

In a third aspect, the invention provides a use of a method according to the first aspect of the invention, and for obtaining a hollow object with an internal surface comprising a coating according to the second aspect of the invention.

In an embodiment of the invention, the coating is utilized as a gas permeation barrier, which is particularly crucial in the context of the development of hydrogen technologies. One significant application is coating the inner surface of hollow objects used for hydrogen distribution to prevent embrittlement of the hollow object. This is considered a significant challenge in hydrogen transportation and storage, and the development of effective gas permeation barriers is of great importance. The gas permeation barrier coating can be engineered to have optimized thickness, composition, and adhesion to suit the specific requirements of the application. It can provide reliable protection against gas permeation, minimizing the risk of embrittlement or other adverse effects on the pipe or substrate material, and ensuring the integrity and performance of the coated component. This gas permeation barrier application has potential uses in various industries, including hydrogen fuel cells, energy storage, and gas distribution systems, among others.

In an embodiment of the invention, the coating serves as a highly effective solution for corrosion resistance. Unlike traditional wet coating options, this innovative method offers the advantage of being solvent-free, making it particularly suitable for developing anti-corrosion coatings within hollow objects. Corrosion resistance is a critical requirement in various industries where for example pipelines are used to transport fluids or gases. The traditional approach of using wet coatings, which involve the use of solvents, can have environmental and safety implications, as solvents may release harmful fumes and contribute to air pollution. Additionally, solvent-based coatings may require additional time for drying and curing processes, leading to longer production cycles and increased costs. However, when utilized as a corrosion resistance coating, the need for solvents is eliminated, making it an environmentally friendly option that minimizes emissions and reduces the risk of health hazards. Moreover, the absence of solvents allows for faster drying and curing, enabling more efficient production processes and shorter lead times. The solvent-free anti-corrosion coating can be applied to the inner surfaces of hollow objects, such as pipes. The coating acts as a barrier, preventing corrosive substances from coming into contact with the pipe surface, thereby significantly reducing the risk of corrosion and extending the lifespan of the pipes. In fact, it may even enhance the protective properties of the coating, as it eliminates the potential for solvent-related issues, such as uneven coverage or poor adhesion.

In an embodiment of the invention, the coating serves as a highly effective solution for surface energy modifications. This innovative method can be applied to various applications where the objective is to enhance the fluid-sliding ability on pipe walls, such as in injectors or in the food industry. Coatings with highly hydrophilic or hydrophobic properties can be advantageously deposited using this method. Surface energy modifications are crucial in numerous industries where the interaction between fluids and surfaces plays a significant role. For example, in injectors, coatings with specific surface properties can optimize the flow of fluids, improving their performance and efficiency. Similarly, in the food industry, coatings with tailored surface energy characteristics can enhance the processing and handling of food products, ensuring smooth and efficient operations. Highly hydrophilic coatings can be deposited to promote wetting of fluids on the pipe walls, reducing friction and improving fluid flow. On the other hand, highly hydrophobic coatings can be applied to repel fluids, minimizing adhesion, and reducing fouling or build-up on the pipe walls. Additionally, the coating can be customized to exhibit other desired surface energy properties, such as oleophobic, amphiphilic, or superhydrophobic properties, depending on the specific application requirements. This versatility in surface energy modifications makes the coating highly adaptable to a wide range of industrial applications where fluid interactions with surfaces are critical. Furthermore, the coating can be uniformly applied to the interior surfaces of hollow objects, such as pipes, ensuring consistent and durable surface energy modifications. The precise deposition process allows for controlled and uniform coverage, enabling reliable and effective performance of the coating over time.

In an embodiment of the invention, the coating serves as a highly effective solution for erosion resistance. This can be utilized to protect surfaces from erosion caused by solid particle impact, which can occur in various industrial applications, such as in aircraft diffusers. Erosion is a significant concern in many industries where surfaces are subjected to high-velocity impacts of solid particles, resulting in gradual wear and damage over time. For instance, in aircraft diffusers, which conduct air to the combustion chamber through numerous narrow gas inlets arranged around a circular frame, erosion caused by dust particles present in the air can result in an increase in gas inlet diameter, leading to potential damage to the aircraft engine. The erosion resistance coating provides a robust protective layer that effectively resists erosion from solid particle impacts. The composition of the coating is designed to withstand high-velocity impacts and prevent wear, reducing the potential for damage and extending the lifespan of critical components. Furthermore, the precise deposition process allows for uniform coverage of the coating on the surfaces, ensuring comprehensive protection against erosion across the entire surface area. The coating adheres firmly to the substrate, maintaining its erosion resistance properties even under challenging conditions. In addition to aircraft diffusers, this erosion resistance coating can also find applications in other industries where surfaces are exposed to solid particle impacts, such as in gas turbines, pumps, and other high-velocity flow systems. By providing reliable protection against erosion, the coating can help mitigate costly maintenance, repair, and replacement of damaged components, resulting in increased operational efficiency and reduced downtime.

The invention is further described by the following non-limiting examples which further illustrate the invention, and are not intended to, nor should they be interpreted to, limit the scope of the invention.

DESCRIPTION OF FIGURES AND EXAMPLES

With as a goal illustrating better the properties of the invention the following presents, as an example and limiting in no way other potential applications, a description of a number of preferred applications of the method for examining the state of the grout used in a mechanical connection based on the invention.

The following numbering refers to:

1. Hollow object
2. Internal surface of the hollow object
3. Cylindrical electrode
4. Reaction chamber
5. Target material A
6. Target material B
7. Target material C
8. Sub-electrode A
9. Sub-electrode B
10. Sub-electrode C
11. Coating 1
12. Coating 2
13. Coating 3

In most cases, the target materials A 5, B 6, and C 7 used for the coating process correspond to the same materials as the cylindrical electrode 3. This means that a wire of the respective target material is utilized, and different materials are welded together to form a wire with multiple targets. The use of a wire consisting of different target materials allows for efficient and convenient deposition of various coatings. By controlling the relative movement between the cylindrical electrode 3 and the hollow object 1, it becomes possible to deposit layers of different materials onto the internal surface. This technique enables the creation of multilayered coatings with distinct properties and compositions. It is worth noting that this approach contributes to the versatility and flexibility of the coating process. It enables the deposition of coatings with varying material compositions, leading to enhanced functionality and performance of the coated hollow object 1.

It is further important to clarify that in certain cases, the hollow object 1 can also function as the reaction chamber. In some configurations, such as those depicted in Figures 2-4, a separate reaction chamber exists alongside the hollow object 1. This dedicated reaction chamber is designed to facilitate the coating process by providing controlled conditions for the deposition of the target material onto the internal surface of the hollow object 2. The cylindrical electrode 3 and the target materials are positioned within this reaction chamber, and the coating process occurs within this confined space. However, there are situations where the hollow object 1 itself can act as the reaction chamber. In such cases, the coating process takes place directly within the internal volume of the hollow object 1, eliminating the need for a separate reaction chamber. This can simplify the setup and potentially offer advantages in terms of efficiency and coating quality.

In figure 1, the hollow object 1 is shown with its internal surface 2 visible. Additionally, a cylindrical electrode 3, functioning as the cathode, is positioned coaxially with respect to the hollow object 1, which serves as the anode. The cylindrical electrode 3 and the internal surface of the hollow object 2 are separated by an average distance labeled as $D_{e,s}$. This depiction emphasizes the precise coaxial alignment of the cylindrical electrode 3 in relation to the hollow object 1, as a notable aspect of the invention.

Figure 2 shows a longitudinal section of a reaction chamber 4, showcasing an embodiment of the present invention wherein a hollow object 1 to be coated is inserted. Notably, the hollow object 1 comprises a cylindrical electrode 3 that functions as the cathode, while the internal surface of the hollow object 2 serves as the anode. The cylindrical electrode 3 acts as cathode to which the electric field is applied for igniting a plasma for deposition of the target material thereof on the internal surface hollow object 2 is provided. The cylindrical electrode 3 is positioned coaxially within the hollow object 1. The cylindrical electrode 3 has a single type of target material evenly distributed over the entire outer surface of the electrode.

The cylindrical electrode 3 has a length which is equal to the length of hollow tube. This allows for the cylindrical electrode 3 to be fixed or attached to holding means within the reaction chamber 4 for the cylindrical electrode 3 to stay in place. The cathode allows the generation of the plasma along the entire length of the hollow object 1, resulting in the simultaneous coating of the entire internal surface of the hollow object 2. Although a horizontal set-up is shown, the set-up, i.e., the positioning hollow object 1 and the cylindrical electrode 3 in the reaction chamber 4 can also be vertical or at any other angle.

Figure 3 shows a longitudinal section of a reaction chamber 4 and a hollow object 1 having an internal surface 2 to be treated defining an internal volume. Further shows this figure a cylindrical electrode 3, functioning as the cathode, and it is utilized to generate an electric field that ignites a plasma for depositing the target material 5 onto the internal surface of the hollow object 2. The cylindrical electrode 3 is positioned coaxially with the hollow object 1 and is coated with a single type of target material 5 that is evenly distributed over its entire outer surface.

The length of the cylindrical electrode 3, is typically designed to match or exceed the length of the hollow tube being coated. For opened tubes, the cylindrical electrode 3 is at least equal in length to ensure comprehensive coverage. In fact, it is common practice for the electrode to be longer than the tube itself to guarantee uniform coating throughout. However, Figure 3 presents a specific scenario depicting a shorter cylindrical electrode 3. This arrangement is specifically employed for semi-opened tubes where the target material cannot pass through the restricted opening. It is important to note that this particular case is an exception, and in all other situations, the cylindrical electrode 3 aligns with or surpasses the length of the hollow tube to facilitate a complete and uniform coating process.

It should be mentioned that the following information regarding relative movement is not applicable when using a single target, as in our case. However, it is relevant for multi-target setups, as shown in Figure 4. To achieve a uniform coating on the internal surface of the hollow object 2, the cylindrical electrode 3 and the hollow object 1are arranged to move relative to each other while maintaining their coaxial position. This relative movement can involve the cylindrical electrode 3 moving alone, or the hollow object 1 moving alone, or both the cylindrical electrode 3 and the hollow object 1 moving simultaneously.

During the deposition process, the cylindrical electrode 3 can advantageously move along the central axis of the hollow object 1. If both the cylindrical electrode 3 and the hollow object 1 are moved, they can move in the same direction at different speeds, or in opposite directions at the same or different speeds. This allows for the creation of zones with varying plasma discharge densities on the internal surface of the hollow object 2. Specifically, the highest plasma density is generated at the portion of the internal surface 2 that is closest to, or at the minimal distance from, the electrode. On the other hand, lower plasma density zones are created at portions of the internal surface 2 that are located further away from the electrode.

In Figure 3, it should be noted that the depicted configuration is specifically designed for coating the inner part of a semi-opened tube, such as for example a clarinet, where access to the interior is limited. In this particular scenario, the cylindrical electrode 3 shown is shorter than the hollow object 1 to accommodate the shape of the tube. However, it is important to emphasize that for any other coating application, where the hollow object 1 is fully accessible, the cylindrical electrode 3 should be at least as long as the length of the object to ensure uniform and effective coating throughout its entire surface. This consideration ensures optimal coating deposition and maintains consistency across different coating processes.

Figure 4 illustrates a longitudinal section of a reaction chamber 4 and a hollow object 1 to be coated. A hollow object 1 has an internal surface 2 that requires treatment, and it encompasses an internal volume. A cylindrical electrode 3, serving as the cathode where an electric field is applied to generate plasma for deposition of the target material 5, is positioned coaxially with the hollow object 1, aligned with its central axis.

The cylindrical electrode 3 comprises of three sub-electrodes 8, 9, 10 that are arranged in series, offering advantages, particularly for achieving specific coating designs and optimizing efficiency. One of the advantages is the ability to create a chemical composition grading within the hollow object 1 when the targets and hollow object 1 remain stationary relative to each other. This means that different sections of the hollow object 1 can be coated with different materials, resulting in a graded composition. This grading can enhance the material's properties and performance.
Another advantage is the ability to design multilayered coatings of different materials, such as A, B, and C, as depicted in Figure 5. This is achieved when the targets and hollow object 1 move relative to each other during the coating process. The sub-electrodes, working in series, facilitate the controlled deposition of each material layer, allowing for the creation of complex coatings with desired properties.

By utilizing the multi-component electrode configuration, the coating process becomes more efficient, saving time compared to performing three separate deposition steps with different electrodes. Moreover, the risk of misalignment or positioning errors is reduced since the number of operations is minimized.

In this figure, the sub-electrodes 8, 9, 10 comprises different target material (target material A 5, target material B 6, target material C 7), enabling the deposition of multi-layer coatings with varying compositions along the internal surface of the hollow object 2. It should be noted that they also can comprise the same target material.

It should be further emphasized that while Figure 4 illustrates a cylindrical electrode 3 that is of equal length to the hollow object 1, the cylindrical electrode 3 can also have a length shorter or longer than the hollow object 1. When the cylindrical electrode 3 is longer than the hollow object 1, it enables the use of sub-electrodes 8, 9, 10 with different target materials. This configuration facilitates the deposition of coatings with varying compositions along the length of the hollow object 1. Additionally, it is important to note that longer wires of a single material are commonly utilized to ensure a uniform coating, even on the edges of the hollow object 1. This approach helps maintain consistency and quality in the deposited coatings. Furthermore, having the centering piece positioned outside the hollow object 1, as depicted in the accompanying drawing, allows for the plasma to remain undisturbed, contributing to the effectiveness and efficiency of the coating process.

In addition, the average distance $D_{e,s}$ between the cylindrical electrode 3 and the internal surface of the hollow object 2 is prominently visible in figure 1 to 4, as it is a crucial parameter in the coating process according to the embodiment of the present invention. This emphasizes the significance of the precise alignment and separation of the cylindrical electrode 3 and the internal surface of the hollow object 2 for the coating process.

In Figure 5, a detailed schematic of a coated hollow object 1 is depicted in longitudinal section. The internal surface of the hollow object 2 has been coated with multiple layers of different coating materials, identified as layers 11, 12, and 13. These layers form a multi-coating structure on the internal surface of the hollow object 2.

Figure 6 show a longitudinal section of a coated hollow object 1, showcasing an embodiment of the invention. The coated object is a hollow tube or cylinder, and the section cut through the tube reveals its internal surface, which has been coated with a single target material 5. The coating 11 on the internal surface of the hollow object 2 appears as a uniform and continuous layer, covering the entire inner surface of the hollow object 1.

The present invention will now be further exemplified with reference to the following example. The present invention is in no way limited to the given example or to the embodiments presented in the figures.

Example 1: a coated hollow object.

The coated hollow object, as shown in figure 6, is a small diameter tube with an internal diameter of 2 mm and a length of 50 mm. The objective of the coating process was to deposit a titanium nitride (TiN) coating onto the internal surface, which is a common tribological coating known for its high hardness and wear resistance properties.

To achieve the desired coating, a physical vapor deposition (PVD) technique called sputtering was employed. The configuration involved a cylindrical electrode, acting as the cathode, positioned within the tube in a coaxial manner to ensure uniform thickness distribution. In this case, a titanium (Ti) target material was used. To promote the formation of the TiN coating, pure nitrogen gas was injected into the chamber during the sputtering process. The nitrogen plasma interaction with the sputtered Ti atoms resulted in the desired TiN coating on the internal surface of the tube. The tube was configured as an anode, and an electric field was applied to the cylindrical electrode, acting as a cathode.

A working pressure of 5 Torr was maintained in the reaction chamber, and the power was set to 200W with a frequency of 250KHz. The pulse duration was set to 1600ns, ensuring efficient sputtering of the target material onto the internal surface of the tube.

After the coating process was completed, the coated object was evaluated for coating quality and homogeneity. Cross-sections of the coated tube were prepared using standard metallographic techniques. The cross-sections were then observed using scanning electron microscopy (SEM) to assess the coating thickness, morphology, and adhesion to the substrate. The SEM images showed a uniform and dense coating with a thickness of approximately 1 μm, adhering well to the entire internal surface of the tube. The coating exhibited a smooth and homogeneous morphology, indicative of a high-quality coating.

In addition, light microscopy (LM) was also used to observe the coated object for any visible defects, such as cracks or voids. The LM images showed a visually uniform and defect-free coating, confirming the high-quality and uniformity of the coating obtained with the given parameters.

Overall, the coated object obtained with the parameters of 5 Torr working pressure, 200W power, 250KHz frequency, and 1600ns pulse duration exhibited a uniform, dense, and high-quality coating on the entire internal surface of the small diameter tube, as evaluated by SEM and LM observations.

The present invention is in no way limited to the embodiments described in the examples and/or shown in the figures. On the contrary, methods according to the present invention may be realized in many different ways without departing from the scope of the invention.

CLAIMS

1. Method for PVD coating an internal surface of a hollow object, wherein the internal surface of the hollow object defines an internal volume, the method comprising the steps of:
    a. providing a cylindrical electrode having a radial outer surface, said cylindrical electrode comprising a target material, wherein said radial outer surface comprises said target material, within the internal volume of the hollow object, preferably coaxially positioned for a uniform coating, wherein said cylindrical electrode and said internal surface of the hollow object are separated by an average distance $D_{e,s}$ of at least 0.5 mm and at most 20 mm; and
    b. generating an electric field between the cylindrical electrode and the internal surface of the hollow object, with the cylindrical electrode serving as a cathode and the hollow object serving as an anode, wherein a product of a working pressure and the average distance $D_{e,s}$ lies between 0.01 Torr.cm and 10 Torr.cm.

2. Method according to claim 1, **characterized in that,** the target material forms a continuous and uniform radial outer surface of the cylindrical electrode.

3. Method according to claim 1 or 2, **characterized in that,** the cylindrical electrode and hollow object are configured to move relative to one another, to allow for the coating of tubes or continuous operation, wherein the movement is parallel to maintain the coaxial positioning of the cylindrical electrode within the internal volume of the hollow object.

4. Method according to according to any of the previous claims 1 to 3, **characterized in that,** wherein the cylindrical electrode comprises a plurality of sub-electrodes arranged in series for achieving a multilayer coating, wherein each sub-electrode comprises the target material, preferably the target material of at least two of the plurality of sub-electrodes is different.

5. Method according to claim 4, **characterized in that,** the sub-electrodes can be sequentially activated and deactivated to deposit different layers of material onto the internal surface of the hollow piece.

6. Method according to any of the previous claims 1 to 5, **characterized in that,** the target material is chosen from a list of: a metal, a metal alloy, a ceramic material, and combinations thereof.

7. Method according to any of the previous claims 1 to 6, **characterized in that,** a power density applied to the cathode is between 0.01 W/cm² and 50 W/cm², preferably between 1.0 W/cm² and 10 W/cm², and more preferably between 2.5 W/cm² and 9.0 W/cm².

8. Method according to any of the previous claims 1 to 7, **characterized in that,** an average current density applied to the cathode is between 0.001 A/cm² and 10 A/cm², preferably between 0.002 A/cm² and 1 A/cm², preferably between 0.003 A/cm² and 0.05 A/cm², and even more preferably between 0.004 A/cm² and 0.03 A/cm².

9. Method according to any of the previous claims 1 to 8, **characterized in that,** a gas, provided in the internal volume, comprises an inert gas, a reactive gas or a combination thereof; wherein the inert gas is selected from a group comprising helium, neon, argon, krypton; wherein the reactive gas is selected from a group comprising nitrogen, oxygen, methane, ammonia or acetylene, preferably the inert gas is argon and the reactive gas is selected from the group of nitrogen, oxygen or acetylene.

10. Method according to any of the previous claims 1 to 9, **characterized in that,** the method comprises a step of pre-treating the internal surface of the hollow object prior to depositing the target material onto the internal surface, wherein pre-treating the internal surface of the hollow object comprises a cleaning and/or an etching step, preferably plasma assisted etching.

11. Method according to claim 10, **characterized in that,** the plasma assisted etching comprises the steps of:
    - passing an etching gas through the reaction chamber, thereby providing the etching gas in the internal volume of the hollow object; and
    - applying a second electric field to the hollow object, with the cylindrical electrode serving as the anode and the hollow object serving as the cathode, to activate the etching gas and generate an etching plasma.

12. Method according to claim 11, **characterized in that,** the etching gas is selected from a group comprising argon, helium, nitrogen, oxygen, methane, ethylene, nitrogen dioxide or nitrous oxide.

13. Method according to any of the previous claims 1 to 12, wherein the method is conducted by diode sputtering.

14. A hollow object with an internal surface comprising a PVD coating, **characterized in that,** said hollow object has an internal diameter smaller than 5 cm, the coating has a thickness between 0.01 µm and 50 µm**, and** a relative deviation of the thickness of the coating is at most 20%.

15. A hollow object with an internal surface comprising a coating according to claim 14, **characterized in that,** a ratio of a length of the hollow object to its internal diameter is at least 10.

16. Use of a method according to at least one of previous claims 1 to 13, for obtaining a hollow object with an internal surface comprising a coating according to one of the previous claims 14 and 15.

FIGURES

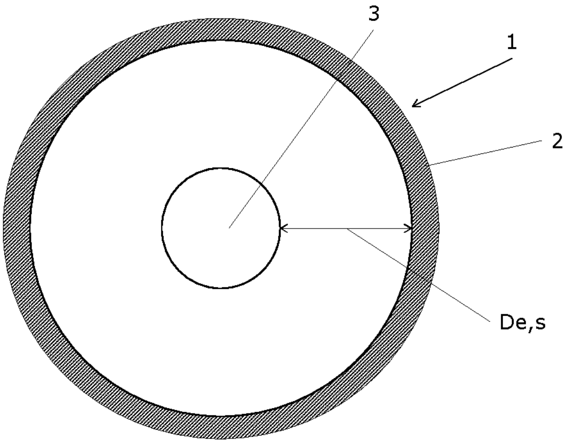

FIG 1.

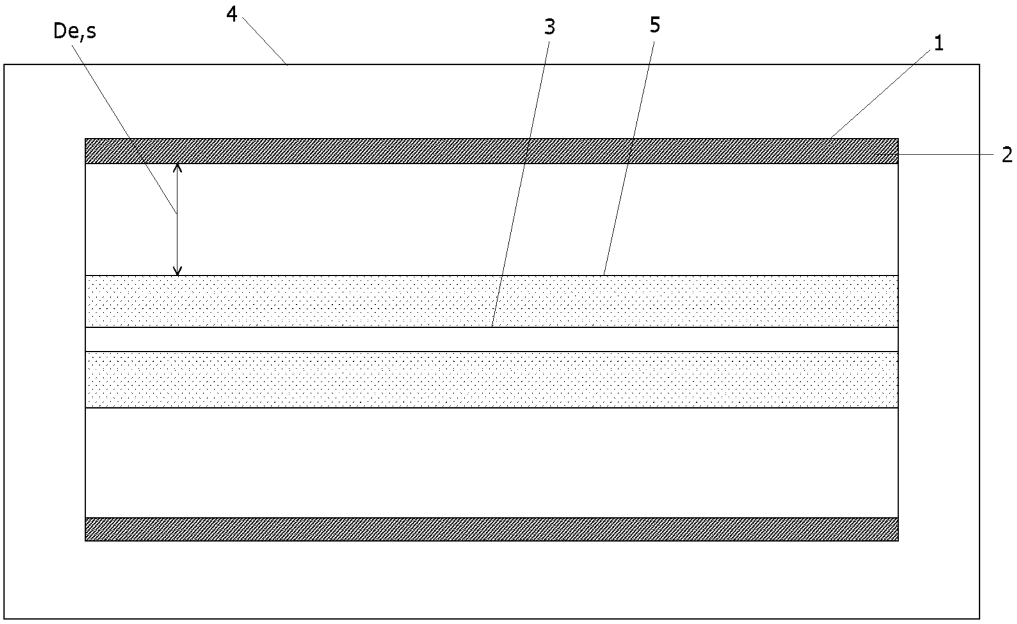

FIG 2.

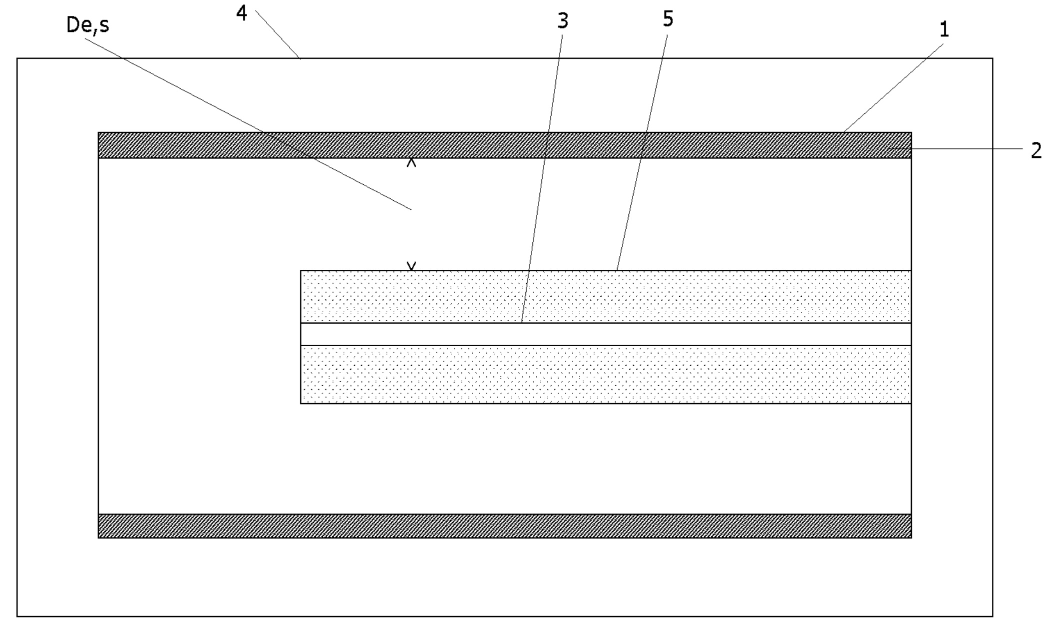

FIG 3.

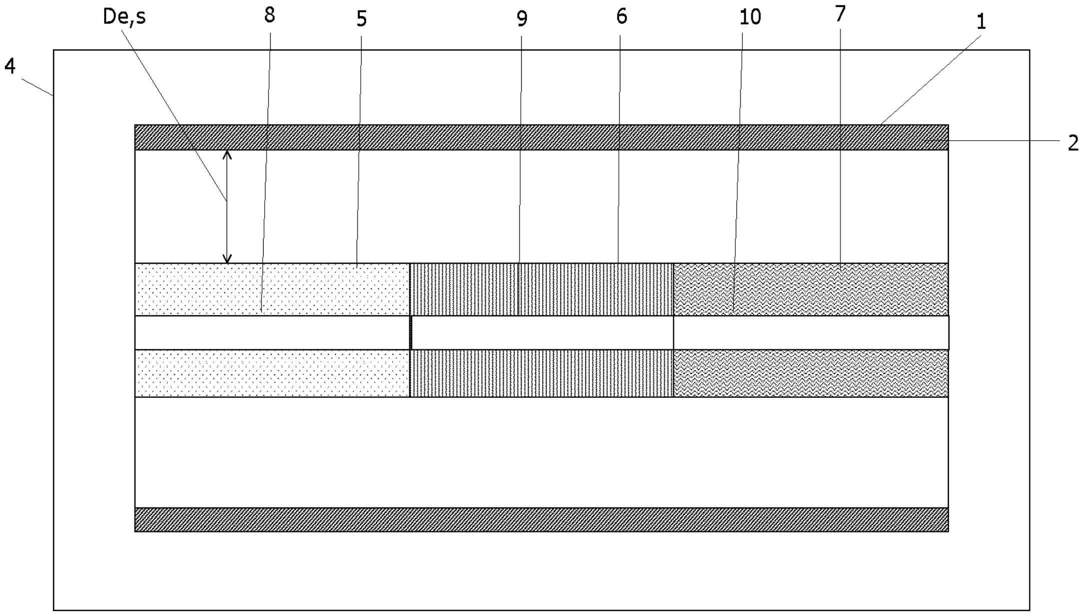

FIG 4.

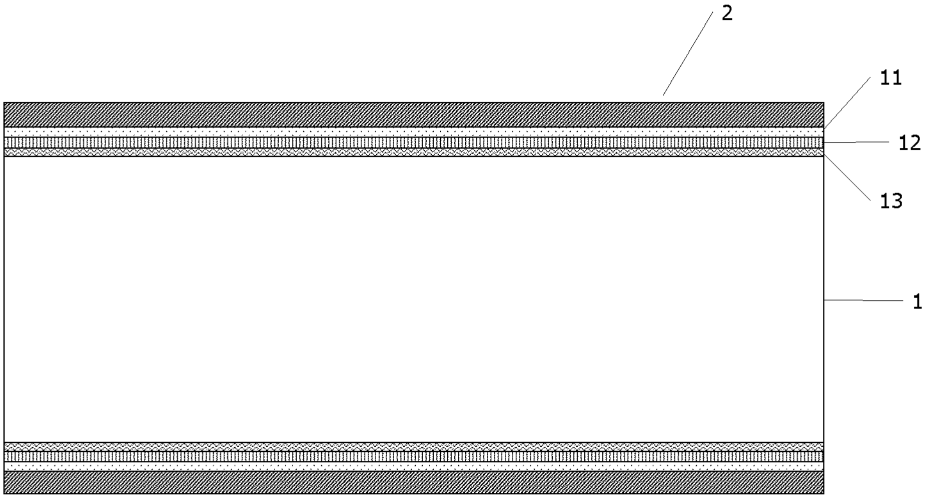

FIG 5.

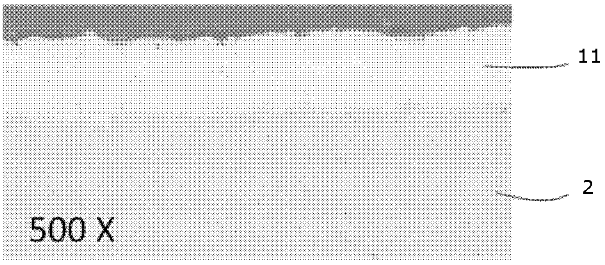

FIG 6.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/065770

A. CLASSIFICATION OF SUBJECT MATTER

INV. C23C14/04 H01J37/32 C23C14/00 C23C14/02 C23C14/34
C23C14/56 C23C14/16

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 H01J

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2017/051393 A1 (HAN SEUNG HEE [KR] ET AL) 23 February 2017 (2017-02-23) paragraphs [0017], [0019], [0022], [0076] - [0078], [0083]; figure 1 -----	1,2,4-7, 9,13-16
X	US 2006/076231 A1 (WEI RONGHUA [US]) 13 April 2006 (2006-04-13) paragraphs [0034], [0035], [0037], [0040], [0044], [0046]; claims 28,37,42,45,46; figure 1 -----	1,2,6,8, 9,13-16
X	WO 2022/261684 A1 (PLASMATERIA GMBH [AT]) 22 December 2022 (2022-12-22) claims 1,9,19,22; figures 1-3 -----	1-3,6, 9-16

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

☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2024/065770

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