

Corrosion Resistant Carbon Coatings

Introduction

This present invention relates to improved corrosion resistant carbon coatings and methods for producing such coatings.

Background to the Invention

A large variety of deposition techniques are used to coat substrates. Vapor deposition technology is typically used to form thin film deposition layers in various types of applications, including microelectronic applications and heavy-duty applications. Such deposition technology can be classified in two main categories. A first category of such deposition technology is known as Chemical Vapor Deposition (CVD). CVD generally refers to deposition processes occurring due to a chemical reaction. Common examples of CVD processes include semiconducting Si layer deposition, epitaxy and thermal oxidation.

A second category of deposition is commonly known as Physical Vapor Deposition (PVD). PVD generally refers to the deposition of solid substances occurring as a result of a physical process. The main concept underlying the PVD processes is that the deposited material is physically transferred onto the substrate surface via direct mass transfer. Typically, no chemical reaction takes place during the process and the thickness of the deposited layer is independent of chemical reaction kinetics as opposed to CVD processes.

Sputtering is a known physical vapor deposition technique for depositing compounds on a substrate, wherein atoms, ions or molecules are ejected from a target material (also called the sputter target) by particle bombardment so that the ejected atoms or molecules accumulate on a substrate surface as a thin film.

Another known physical vapor deposition technique is cathodic vapor arc (CVA) deposition methods. In this method, an electric arc is used to vaporize material from a

cathode target. Consequently, the resulting vaporized material condenses on a substrate to form a thin film of coating.

Amorphous carbon is a free, reactive form of carbon which does not have a crystalline form. Various forms of amorphous carbon films exist and these are usually categorised by the hydrogen content of the film and the $sp^2:sp^3$ ratio of the carbon atoms in the film.

In an example of the literature in this field, amorphous carbon films are categorised into 7 categories (see table below taken from "Name Index of Carbon Coatings" from Fraunhofer Institut Schich- und Oberflächentechnik):

Amorphous Carbon Films						
Hydrogen-Free			Hydrogenated			
Unmodified		Modified	Unmodified		Modified with	
		With metals			Metals	Non-metals
sp^2	sp^3	sp^2	sp^2 or sp^3	sp^3	sp^2	sp^2
Hydrogen-free amorphous carbon	Tetrahedral, hydrogen-free amorphous carbon	Metal-containing, hydrogen-free amorphous carbon	Hydrogenated amorphous carbon	Tetrahedral, hydrogenated amorphous carbon	Metal-containing, hydrogenated amorphous carbon	Non-metal containing hydrogenated amorphous carbon
a-C	ta-C	a-C:Me	a-C:H	ta-C:H	a-C:H:Me	a-C:H:X

Tetrahedral hydrogen-free amorphous carbon (ta-C) is characterised in that it contains little or no hydrogen (less than 5%mol, typically less than 2%mol) and a high content of sp^3 hybridised carbon atoms (typically greater than 80% of the carbon atoms being in the sp^3 state).

Whilst the term "diamond-like carbon" (DLC) is sometimes used to refer to all forms of amorphous carbon materials, the term as used herein refers to amorphous carbon materials other than ta-C. Common methods of DLC manufacture use hydrocarbons (such as acetylene), hence introducing hydrogen into the films (in contrast to ta-C films in which the raw material is typically hydrogen free high purity graphite).

In other words, DLC typically has an sp^2 carbon content of greater than 50% and/or a hydrogen content of 20%mol and above. The DLC may be undoped or doped with metals or non-metals (see table above).

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Tetrahedral amorphous carbon coatings have high hardness and low friction coefficient, and are excellent wear-resistant coatings. At the same time, the ta-C can maintain its stability over long time periods in harsh environments (such as acidic or alkaline conditions) and therefore has broad prospects in the development of anti-corrosion applications. However, due to small defects in the PVD processes, complete coverage of substrate is not achieved and small "pin-holes" in the ta-C film make the underlying substrate susceptible to corrosion. This might happen because e.g. of the presence of large (relatively speaking) dust particles in the very thin coatings. Pin holes can be reduced in a clean room but not absolutely avoided.

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In many applications, parts are required to have both the strength of steel and long-term use in harsh environments (such as acid, alkali or seawater) while maintaining their friction and wear properties. It is known for manufacturers of smartphones to test devices by immersion in swimming pool water for up to a week. This is a tough test and known coatings fail this test at too high a rate. Separately, coatings on electrodes require virtual absence of pin holes for corrosion free operation; few coatings meet this criterion.

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At present, whilst certain types of stainless steel (such as 316L) possess good corrosion resistance, the hardness of this material is low and it therefore cannot be used for high-strength structural parts. Meanwhile, high-strength structural steels (such as 40Cr) are generally prone to rust.

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Conventional surface treatment processes (nitriding, carburizing, etc.) confer limited corrosion resistance on steel. Moreover, due to problems such as the temperature of the process, such processes cannot be used in the field of precision parts (as they result in problems such as brittle fracture, etc). In addition, for certain coatings an electrochemical

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reaction (referred to as the “small battery effect”) occurs between the coating and the substrate which causes corrosion of the coating and/or substrate. Lastly, some PVD-deposited coatings are simply not very corrosion resistant.

- 5 WO 2009/151404 discloses applying coatings using CVA methods followed by a thick CVD layer. Corrosion resistance of the coatings is not addressed.

WO 2009/151404 discloses applying coatings using CVA and PVD (but not CVA) where the thickness of the CVA layer is greater than the thickness of the PVD (non CVA) layer.

- 10 Again, corrosion resistance of the coatings is not addressed.

US 2007/0181843 describes a valve component for a faucet coated with a first layer of a material provided in order to improve the abrasion resistance of the substrate and a second layer of an amorphous diamond material. EP1505322 describes a sliding member coated with a carbon coating. The carbon coating has an outermost surface portion lower in hydrogen content than a remaining portion thereof. Both of these documents are concerned with providing coatings which provide reduce wear resistance rather than corrosion resistant coatings.

- 20 There therefore exists the need for thin, corrosion resistant carbon coatings.

An object of the present invention is to provide coatings that are an alternative to and preferably offer improvements in relation to corrosion resistance, addressing one or more problems identified in the art.

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The Invention

The inventor of the present application has found that carbon coatings with one or more layers of a first material (e.g. DLC) deposited by CVD and a second material (e.g. ta-C) deposited by FCVA have good hardness and wear resistance as well as being more resistant to corrosion compared to films formed by CVA-deposition alone. More

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generally, it is found that a layer deposited via CVD as a component of a coating comprising PVD-deposited layers provides a coating with corrosion resistance.

Accordingly, the present invention provides a substrate with a multi-layer coating,
5 comprising in order:

- i) the substrate;
- ii) a seed layer;
- iii) a barrier layer deposited via a CVD method; and
- iv) a functional layer deposited via a PVD method.

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Suitably, and as illustrated in examples, the present invention provides a substrate with a multi-layer coating, comprising in order:

- i) the substrate;
- ii) a seed layer;
- 15 iii) a barrier layer comprising DLC deposited via a CVD method; and
- iv) a functional layer comprising ta-C.

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Similarly provided is a coating for a substrate, comprising in order:

- i) a seed layer;
- 20 ii) a barrier layer deposited via a CVD method; and
- iii) a functional layer deposited via a PVD method.

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Suitably, the coating may comprise

- i) a seed layer;
- 25 ii) a barrier layer comprising DLC deposited via a CVD method; and
- iii) a functional layer comprising ta-C.

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Alternatively, the coating may comprise:

- i) a seed layer;
- 30 ii) an intermediate layer comprising ta-C;
- iii) a barrier layer comprising DLC deposited via a CVD method; and

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- iv) a functional layer comprising ta-C.

Also provided is a method of coating a substrate, comprising

- 5 i) providing a substrate;
 ii) depositing onto the substrate a seed layer;
 iii) depositing onto the substrate a layer via a CVD method; and
 iv) depositing onto the substrate of a layer via a PVD method.

10 The coatings of the invention may comprise multiple alternating layers of CVD-deposited layers and PVD-deposited layers (i.e. alternating barrier layers and functional layers). The CVD-deposited layers act as barrier layers to protect the underlying substrate from corrosion.

15 Thus, the invention enables coating of a substrate with a coating that shows good hardness and wear resistance as well as good corrosion resistance, as illustrated by the testing of embodiments of the invention described in more detail below.

Detailed Description of the Invention

20 As discussed above, the term “tetrahedral amorphous carbon” (ta-C) as used herein refers to amorphous carbon having a low hydrogen content and a low sp^2 carbon content.

25 Ta-C is a dense amorphous material described as composed of disordered sp^3 , interlinked by strong bonds, similar to those that exist in disordered diamond (see Neuville S, “New application perspective for tetrahedral amorphous carbon coatings”, QScience Connect 2014:8, <http://dx.doi.org/10.5339/connect.2014.8>). Due to its structural similarity with diamond, ta-C also is a very hard material with hardness values often greater than 30 GPa.

30 For example, the ta-C may have a hydrogen content less than 10%, typically 5% or less, preferably 2% or less (for example 1% or less). The percentage content of hydrogen provided here refers to the molar percentage (rather than the percentage of hydrogen by

mass). The ta-C may have an sp^2 carbon content less than 30%, typically 20% or less, preferably 15% or less. Preferably, the ta-C may have a hydrogen content of 2% or less and an sp^2 carbon content of 15% or less. The ta-C is preferably not doped with other materials (either metals or non-metals).

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By contrast, the term “diamond-like carbon” (DLC) as used herein refers to amorphous carbon other than ta-C. Accordingly, DLC has a greater hydrogen content and a greater sp^2 carbon content than ta-C. For example, the DLC may have a hydrogen content of 20% or greater, typically 25% or greater, for example 30% or greater. The percentage
10 content of hydrogen provided here again refers to the molar percentage (rather than the percentage of hydrogen by mass). The DLC may have an sp^2 carbon content of 50% or greater, typically 60% or greater. Typically, the DLC may have a hydrogen content of greater than 20% and an sp^2 carbon content of greater than 50%. The DLC may be undoped or doped with metals and/or non-metals.

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The invention advantageously provides deposited coatings via PVD methods, for example ta-C coatings deposited via FCVA, that are hard and have high wear resistance, and now good corrosion resistance as a consequence of the one or more intermediate CVD-deposited layer(s).

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Accordingly, the present invention provides a substrate with a multi-layer coating, comprising in order:

- i) the substrate;
- ii) a seed layer;
- 25 iii) a barrier layer deposited via a CVD method; and
- iv) a functional layer deposited via a PVD method.

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Choice of the substrate material is broad, and many substrates made of a wide range of materials can be coated. The substrate is usually metallic and generally is or comprises
30 a metal or an alloy. Steels are suitable substrates, e.g. steel, stainless steel, HSS, tool steel and alloy steel, Ti or its alloys, Al or its alloys. Ceramics such as Al_2O_3 , ZrO_2 , Si_3N_4 ,

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SiC, and plastics such as PEEK, POM, LCP, ABS, PC are also suitable substrates. Articles are generally made of the substrate and then have a coating of the invention applied / deposited.

- 5 The functional layer (deposited via a PVD method) preferably comprises or consists of ta-C. Typically, the uppermost layer of the coating (i.e. the layer furthest away from the substrate) is a layer comprising ta-C in order to impart the performance of the ta-C on the final coating. Preferably, the functional layers comprising ta-C consist of ta-C.
- 10 The thickness of each of the functional layers is typically from 0.1µm to 3µm, for example from 0.2µm to 2µm, preferably from 0.5µm to 1µm. The functional layers (e.g. those comprising ta-C) are preferably deposited via FCVA.

- The barrier layers typically comprise or consist of DLC and are located between the seed
15 layer and the PVD-deposited (e.g. ta-C-containing) layer(s) and optionally also between adjacent PVD-deposited (e.g. ta-C-containing) layers. The barrier layers preferably consist of DLC. The barrier layers are deposited via a chemical vapour deposition technique. Examples of such techniques include plasma enhanced-CVD and hot filament-CVD. Such techniques are well known to those skilled in the art.

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- It has been found that deposition via CVD results in fewer gaps in the produced coating and this layer grows on top of the substrate avoiding pin holes. CVD provides good coverage of the material being coated and therefore acts as a barrier to corrosion causing substances (e.g. acids). Pin holes in the PVD-deposited layer can be plugged with the
25 CVD-deposited layer.

When the barrier layer comprises or consists of DLC, the DLC is typically not conductive unless doped. An option, therefore, is for the DLC to be metal-doped in order to increase the electric conductivity of the coating. This depends upon the end-use of the coating.

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Coated substrates may comprise multiple alternating barrier layers and functional layers. These are generally deposited in turn, as barrier / functional / barrier / functional etc with the uppermost layer being a hard, functional layer. There may be at least 2, or at least 3 or at least 5 of each. Addition of multiple further layers does not always significantly increase the corrosion resistance, and suitably the coated substrates comprise alternating layers of up to 10 barrier layers and up to 10 functional layers.

When the coating comprises a single barrier layer, the thickness of the barrier layer may be up to 5 μm , preferably up to 2 μm , and generally 1 μm or less or from 0.05 μm to 0.5 μm , for example from 0.07 μm to 0.4 μm or from 0.1 μm to 0.3 μm .

Alternatively, when the coating comprises multiple barrier layers, the thickness of each barrier layer may be reduced compared with the above, and is suitably 1 μm or less, preferably 0.5 μm or less for example 100nm or less, 20nm or less, 10nm or less, 5nm or less or 3nm or less.

Accordingly, the total thickness of all barrier layers within the coating may be up to 5 μm , preferably up to 2 μm , and generally 1 μm or less or 0.05 μm to 0.5 μm , for example from 0.07 μm to 0.4 μm or from 0.1 μm to 0.3 μm .

Barrier layers of this thickness are thick enough to confer sufficient corrosion resistance on the layered coating, but without significantly impacting the overall hardness and/or wear-resistance and/or conductivity of the coatings, these properties being imparted to the coatings by the other, e.g. functional layers. Hence, pin holes in the relatively thicker, functional PVD-deposited layer can be plugged with the relatively thin CVD-deposited layer without adversely impacting upon the properties of the functional layer.

One or more seed layers are included to promote adhesion of the barrier layer to the underlying substrate. The nature of the seed layers will therefore depend on the nature of the substrate. When the substrate is metallic, the seed layer preferably comprises Cr, W, Ti, NiCr, Si or mixtures thereof or combinations of these metals with carbon or

nitrogen. When the substrate is a steel substrate, an example of a preferred material for the seed layer is NiCr and/or Ti. The total thickness of the seed layer(s) is/are typically greater than 0.05µm or greater than 0.3µm and is/are often less than 2µm or less than 1.5µm. Suitable thickness ranges for the seed layer(s) therefore include from 0.05µm to 2µm, for example from 0.1µm to 1µm, preferably from 0.2µm to 0.5µm.

The coating may also comprise an intermediate layer in between the seed layer and the barrier layer. The purpose of the intermediate layer is to improve adhesion between the seed layer and the barrier layer. The intermediate layer may comprise or consist of ta-C and may have a thickness of 0.1µm or more, or 0.2µm or more; the thickness is generally up to 1.5µm, for example up to 1.0µm or up to 0.5µm. When the intermediate layer comprises or consists of ta-C, the intermediate layer may be deposited via a PVD process, such as a cathodic vacuum arc deposition process (e.g. an FCVA process).

The overall thickness of the coating (including e.g. the seed layer(s) and all barrier layers and ta-C-containing layers present) is typically 10µm or less, preferably 5µm or less, for example 3µm or less or 2µm or less.

An aim of the invention is to provide hard coatings, for many applications. Coated substrates of the invention preferably have a coating with a hardness of at least 1000 HV, more preferably 1500 HV or more, or 2000 HV or more. Coatings with a wide range of measured hardness values within these ranges have been made (see examples below), including coatings with hardness of approximately 2300 HV. For different end applications, according sometimes to user choice, different hardness may be appropriate.

Conventional CVD and PVD methods, specifically CVA and FCVA processes, are known and used for a wide range of substrates and the methods of the invention are similarly suitable for coating a wide range of substrates. Solids, both conducting and non-conducting, are generally suitable and seed layers and adhesion layers can be used to improve coating adhesion and strength, and to render surfaces amenable to being

coated. Substrates made of metal, alloy, ceramics and mixtures thereof can be coated. Typically, the substrate is a corrosion-prone substrate, such as steel.

Coatings of the invention can be multilayered and the respective layers may independently be deposited using a range of known and conventional deposition techniques, including CVD, PVD, magnetron sputtering and multi-arc ion plating. Sputtering is one suitable method, especially for the seed layer. PVD is suitably used for the ta-C-containing layers, e.g. CVA. The CVA process is typically a filtered cathodic vacuum arc (FCVA) process, e.g. as described below. Apparatus and methods for FCVA coatings are known and can be used as part of the methods of the invention. The FCVA coating apparatus typically comprises a vacuum chamber, an anode, a cathode assembly for generating plasma from a target and a power supply for biasing the substrate to a given voltage. The nature of the FCVA is conventional and not a part of the invention.

CVD processes can make use of ion sources (including end-hall ion sources, Kaufman ion sources, anode layer sources, hot filament ion sources and hollow cathode ion sources) for the material being deposited. Alternatively, the coating material may be provided as a gas which is then charged/ionised using a power supply (e.g. DC power supply, pulsed DC power supply or RF power supply).

An example of a steel substrate with a multi-layer coating comprises in order:

- i) the steel substrate;
- ii) a seed layer having a thickness from 0.05 μ m to 2 μ m;
- iii) a barrier layer deposited by a CVD method, the barrier layer comprising DLC and having a thickness of 10nm or less; and
- iv) a layer comprising ta-C deposited by CVA and having a thickness of from 0.1 μ m to 3 μ m.

A further example of a steel substrate with a multi-layer coating comprises in order:

- i) the steel substrate;
- ii) a seed layer having a thickness from 0.05 μ m to 2 μ m;

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- iii) a barrier layer deposited by a CVD method, the barrier layer comprising DLC and having a thickness of $2\mu\text{m}$ or less; and
- iv) a layer comprising ta-C deposited by CVA and having a thickness of from $0.1\mu\text{m}$ to $3\mu\text{m}$.

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Yet a further example of a steel substrate with a multi-layer coating comprises in order:

- i) the steel substrate;
- ii) a seed layer having a thickness from $0.05\mu\text{m}$ to $2\mu\text{m}$;
- iii) an intermediate layer comprising ta-C having a thickness of from $0.1\mu\text{m}$ to $1.0\mu\text{m}$;
- iv) a barrier layer deposited by a CVD method, the barrier layer comprising DLC and having a thickness of $2\mu\text{m}$ or less; and
- v) a layer comprising ta-C deposited by CVA and having a thickness of from $0.1\mu\text{m}$ to $3\mu\text{m}$.

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Hardness is suitably measured using the Vickers hardness test (developed in 1921 by Robert L. Smith and George E. Sandland at Vickers Ltd; see also ASTM E384-17 for standard test), which can be used for all metals and has one of the widest scales among hardness tests. The unit of hardness given by the test is known as the Vickers Pyramid Number (HV) and can be converted into units of pascals (GPa). The hardness number is determined by the surface area of the indentation which is tested by a certain load. As examples. Martensite a hard form of steel has HV of around 1000 and diamond can have a HV of around 10,000 HV (around 98 GPa). Hardness of diamond can vary according to precise crystal structure and orientation but hardness of from about 90 to in excess of 100 GPa is common.

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The invention advantageously provides high hardness and wear-resistant ta-C-based coatings. Compared to known ta-C coatings, the coatings of the invention have improved resistance to corrosion due to the presence of the DLC barrier layer(s).

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Brief Description of the Drawings

Fig. 1A shows an uncoated steel substrate (comparative example) following corrosion testing as described in Example 2.

- 5 Fig. 1B shows a ta-C-coated steel substrate (comparative example) following corrosion testing as described in Example 2.

Fig. 1C shows a steel substrate coated with a coating of the invention following corrosion testing as described in Example 2.

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Fig. 1D shows a DLC-coated steel substrate (comparative example) following corrosion testing as described in Example 2.

Detailed Description of the Invention

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Example 1

The protocol for making corrosion resistant films according to the invention is provided below:

- 20 a. A high speed steel (HSS) substrate is first prepared for coating by ultrasonic cleaning with a detergent. The substrate is then rinsed with deionised water and then dried (in accordance with standard cleaning processes used in the vacuum industry).
- b. The cleaned HSS substrate is placed in a vacuum chamber having sputtering, CVD and FCVA targets/sources.
- 25 c. The chamber is pumped down to reduce the pressure to less than 1×10^{-5} Torr (0.00133 Pa), and heated to between 150°C and 200°C.
- d. Ion cleaning is conducted in the chamber in order to activate the surface of the substrate to promote adhesion.
- 30 e. Seed layer deposition: Sputtering, 100°C - 150°C, NiCr targets, layer thickness = 1.0µm.

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- f. Barrier layer deposition: Plasma Assisted CVD, C_2H_2 (flow rate = 100sccm) and Ar (flow rate = 200 sccm), bias voltage = 600V, bias current = 8A, bias duty cycle = 50%; layer thickness = 0.2 μ m.
- g. Functional layer deposition: FCVA, <100°C, solid graphite target, coating thickness = 1.3 μ m.

Sputtering, CVD and FCVA targets and sources are well-known and commercially available.

10 Example 2 - Corrosion Resistance Testing

A salt spray test was used to determine the corrosion resistance of the coatings of the invention (as produced in Example 1) compared to uncoated and DLC coated substrates.

Test materials:

- 15 a. Uncoated high speed steel $W_6Mo_5Cr_4V_2$ substrate (without surface treatment). Hardness = 746.9 HV
- b. Ta-C coated high speed steel $W_6Mo_5Cr_4V_2$. Coating thickness = 2.3 μ m. Hardness = 2212 HV. The coating was prepared according to the method of Example 1, with the omission of barrier layer deposition step (f).
- 20 c. High speed steel $W_6Mo_5Cr_4V_2$ coated with ta-C coating of the invention (see Example 1). Coating thickness = 2.5 μ m. Hardness = 2317 HV
- d. High speed steel $W_6Mo_5Cr_4V_2$ substrate coated with DLC only. Coating thickness = 2.5 μ m. Hardness = 1540 HV.

25 Salt Spray Conditions:

- Salt solution concentration: $(5 \pm 1)\%$ NaCl
- pH = 6.5-7.2
- Salt spray settling rate: (1-2mL) / 80cm²;
- Temperature inside the salt spray box: 35 $\pm$ 2°C;
- 30 • Spray 1 min every 10 minutes;

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Results:

- a) Uncoated – Obvious rust of the surface after 10 minutes (see Figure 1A)
 - b) Ta-C coated – Visible, erasable rust after 18 hours (see Figure 1B). When subjected to a scratch test, the coating showed a critical load of 38.66N.
 - 5 c) Invention – No obvious rust after 100 hours (see Figure 1C). When subjected to a scratch test, the coating showed a critical load of 30.60N.
 - d) DLC coated – No obvious rust after 100 hours (see Figure 1D). When subjected to a scratch test, the coating showed a critical load of 20.22N.
- 10 As an indication of the wear-resistance of the coatings, a Taber abrasion test was conducted on test materials b), c) and d), with the following conditions:
- Instrument: Taber Linear Abraser TLA 5700
 - Abradant: CS-17 Wearaser®
 - Test Load: 1 kg weight
 - 15 • Cycle Speed: 60 cycles/min
 - Stroke Length: 15 mm

No visible scratches were seen on either test material b) and c) following 30,000 cycles of the taber test. However, visible scratches were seen on test material d) following only
20 5,000 cycles of the taber test.

The coatings of the invention therefore show improved corrosion resistance compared to uncoated substrates and substrates coated with DLC alone. The coatings of the invention also have comparable hardness and wear resistance properties to ta-C-only coated
25 substrates and have superior hardness and wear resistance properties compared to DLC-only coated substrates.

Example 3 – Further Protocol

A protocol for is described below for coating a high speed steel substrate with a coating
30 of the invention.

Step 1: First the substrate is cleaned using industrial cleaning agents and ultrasonic cleaning, rinsed with pure water and then dried. Such a cleaning process is commonly used in the vacuum coating industry and is conducted to remove oil stains and dirt on the substrate surface prior to coating.

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Step 2: The substrate is loaded and clamped into the coating chamber and the chamber is heated to a temperature of 130°C and depressurized to a pressure from 1.0×10^{-3} Pa to 4.0×10^{-3} Pa.

10 Step 3: Plasma cleaning is conducted in order to activate the substrate surface for coating (e.g. ion cleaning USES, for example using a linear ion source device as described in Chinese patent application no. 201621474910.4)

15 Step 4: A seed layer is coated onto the activated substrate via a magnetron sputtering process. A negative bias pulse (150V – 600V) is applied to the substrate and a working pressure of Argon of 150sccm to 300sccm is used. The seed layer can be formed from NiCr, Ti, Si, Cr, W or combinations of these metals with carbon or nitrogen. The thickness of the seed layer may be from 0.3µm to 1.5µm.

20 Step 5: Optionally a ta-C intermediate layer is deposited on top of the seed layer. The ta-C is deposited using an FCVA process (e.g. as described in Chinese patent application no. 201621474910.4) using a graphite target and by applying a negative pulse bias of 500V to 2000V to the substrate. The thickness of this ta-C layer is typically from 0.2µm to 1.5µm.

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Step 6: A DLC layer is applied onto the seed layer (if no ta-C intermediate layer is deposited in Step 5) or on top of the ta-C layer (if a ta-C intermediate layer is deposited in Step 5). The DLC is deposited via a plasma-assisted chemical vapour deposition process using argon and a carbon source gas (such as methane, acetylene, ethane or
30 other hydrocarbon gases). Deposition is conducted at a chamber pressure of 0.4 Pa to

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2 Pa with a pulse negative substrate bias of 300V to 800V. The thickness of this layer is typically greater than 0.5µm

Step 7: Finally, a ta-C layer is deposited. The ta-C is deposited using an FCVA process (e.g. as described in Chinese patent application no. 201621474910.4) using a graphite target and by applying a negative pulse bias of 500V to 2000V to the substrate. The thickness of this ta-C layer is typically from 0.4µm to 1.0µm.

Example 4 – Further Coatings

Further coated substrates of the invention were prepared with the following structures, using the protocol described in Example 3.

Coating 4A:

- High Speed Steel Substrate
- NiCr (1.0µm)
- Ti (0.2µm)
- Ta-C (1.0µm)
- DLC (1.0µm)
- Ta-C (0.5µm)

Overall coating thickness is 3.7µm.

Coating 4B:

- High Speed Steel Substrate
- NiCr (1.0µm)
- Ti (0.2µm)
- Ta-C (0.4µm)
- DLC (1.0µm)
- Ta-C (1.0µm)

Overall coating thickness is 3.6µm.

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Coating 4C:

- High Speed Steel Substrate
- NiCr (1.0 μ m)
- 5 • Ti (0.2 μ m)
- Ta-C (0.5 μ m)
- DLC (0.2 μ m)
- Ta-C (0.5 μ m)
- DLC (0.2 μ m)
- 10 • Ta-C (0.5 μ m)

Overall coating thickness is 3.1 μ m.

Claims

1. A metallic substrate with a multi-layer coating, comprising in order:
 - i) the metallic substrate;
 - 5 ii) a seed layer;
 - iii) a barrier layer comprising DLC deposited via a CVD method; and
 - iv) a functional layer comprising ta-C deposited via a PVD method; andwherein the overall thickness of the coating is 5µm or less; wherein the substrate comprises multiple alternating barrier layers and functional layers; and wherein the
10 thickness of each barrier layer is 0.5µm or less.
2. A coated substrate according to claim 1 comprising alternating layers of up to 10 barrier layers and up to 10 functional layers
- 15 3. A coated substrate according to claim 1 or 2 which further comprises an intermediate layer between the seed layer ii) and the barrier layer iii)
4. A coated substrate according to claim 3 wherein the intermediate layer comprises ta-C.
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5. A coated substrate according to any of claims 1 to 4 wherein the total thickness of all barrier layers in the substrate is up to 1.0µm.
6. A coated substrate according to any of claims 1 to 5 wherein the thickness of the
25 functional layer is from 0.1µm to 3µm.
7. A coated substrate according to any of claims 1 to 6 wherein the thickness of the seed layer is from 0.05µm to 2µm.
- 30 8. A coated substrate according to any of claims 1 to 7 wherein the functional layer(s) is/are deposited by FCVA.

9. A coated substrate according to any of claims 1 to 8 wherein the seed layer is formed from Cr, W, Ti, NiCr, Si or mixtures thereof.

5 10. A coated substrate according to any of claims 1 to 9 wherein the substrate is a steel substrate.

11. A coated substrate according to claim 10 wherein the substrate comprises stainless steel, HSS, tool steel or alloy steel.

10 12. A coated substrate according to any of claims 1 to 9 wherein the substrate comprises Ti, an alloy of Ti, Al or an alloy of Al.

13. A coated substrate according to any of claims 1 to 12, comprising at least 2 barrier
15 layers and at least 2 functional layers.

14. A coated substrate according to any of claims 1 to 13, comprising at least 3 barrier layers and at least 2 functional layers.

20 15. A coated substrate according to any of claims 1 to 14, wherein the barrier layer comprising DLC has a hydrogen content of 20% or greater.

16. A coated substrate according to any of claims 1 to 15, wherein the functional layer comprising ta-C has a hydrogen content of less than 10%.

25 17. The metallic substrate with a multi-layer coating according to claim 1 comprising in order:

- i) the metallic substrate wherein the metallic substrate is a steel substrate;
- ii) the seed layer having a thickness from 0.05 μ m to 2 μ m;
- 30 iii) the barrier layer deposited by a CVD method, the barrier layer comprising DLC and having a thickness of 0.5 μ m or less; and

- iv) the functional layer comprising ta-C deposited by CVA and having a thickness of from 0.1 μ m to 3 μ m;

wherein there are multiple alternating barrier layers (iii) and functional layers (iv).

- 5 18. The metallic substrate with a multi-layer coating according to claim 1 comprising in order:

- i) the metallic substrate wherein the metallic substrate is a steel substrate;
- ii) the seed layer having a thickness from 0.05 μ m to 2 μ m;
- 10 iii) an intermediate layer comprising ta-C having a thickness of from 0.1 μ m to 1.0 μ m;
- iv) the barrier layer deposited by a CVD method, the barrier layer comprising DLC and having a thickness of 0.5 μ m or less; and
- v) the functional layer comprising ta-C deposited by CVA and having a thickness of from 0.1 μ m to 3 μ m;

15 wherein there are multiple alternating barrier layers (iv) and functional layers (v).

19. A method of coating a metallic substrate, the method comprising

- i) depositing onto the substrate a seed layer;
- 20 ii) depositing onto the substrate a layer of DLC having a thickness of 0.5 μ m or less via a CVD method; and
- iii) depositing onto the substrate a layer of ta-C via a PVD method; and
- iv) repeating steps ii) and iii).