METHOD FOR REACTIVE SPUTTERING

Abstract: The invention is related to the method of creating protective and functional layers using the PVD method, from a cathode with reduced surface electrical conductivity, by way of application from the working coating source where the principle is that the material is applied to the substrate (6) from the working coating source designed as a rotating working cathode (2) wherein the rotating working cathode (2) is coated during the process from the auxiliary coating source with material with sufficient electrical conductivity where the layer of the coating applied to the surface of the rotating working cathode (2) has greater electrical conductivity than the surface of this rotating working cathode (2) created during the processes without coating of the rotating working cathode using the auxiliary coating source.
with amended claims (Art. 19(1))
FIELD OF THE INVENTION

The invention is related to the method of application, deposition or coating of material, most frequently using a low-voltage arc, or material de-dusting, typically using magnetron sputtering, in cases where the surface conductivity of the cathode is reduced by the so-called cathode poisoning. Material is released from this cathode for deposition on the coated substrate, the surface of which is supposed to be protected and/or functionally treated, and where such degraded, or poisoned (as the case may be) cathode impairs the quality of deposition of the protective and/or functional layers.

BACKGROUND OF THE INVENTION

There are known methods of preparation of abrasion-resistant as well as functional layers using the PVD method in the presence of chemically reacting gas such as oxygen or nitrogen, and also using a combined method of PVD and CVD, in which material is evaporated or de-dusted from the electrode, which is always - in the cases described herein - the cathode, as well as the material, which is applied to the surface of this electrode by the decomposition of gaseous compounds introduced to the equipment at the same time for the purpose of combined application using the PVD and CVD methods, for example during the preparation of the layers containing carbon, e.g., DLC (Diamond-Like-Carbon), either individual or in combination with carbides, nitrides, etc. During the deposition of the respective layer in these cases, the surface of the cathode is poisoned with a polymer, poorly conductive layer, which has negative impact on the further process of deposition.

There are known methods of creating oxide protective or functional layers using the technique of bipolar pulsed Dual Magnetron Sputtering, in which the anode
and cathode are recurrently switched. In most cases, the purpose of these methods is to clean the poisoned anode, coated from the de-dusted cathode, by switching between the anode and the cathode in regular intervals. These methods are known, for example, from documents EP 0462303 and US 6423403.

There are known methods of creating layers (Al,Cr)\(2\theta_3\) using the PVD principle where chromium significantly reduces the deposition temperature and increases abrasion resistance of the layer. Such method is known, for example from a document EP 0513662.

There are also known technologies of application of hard abrasion-resistant layers from rotating cathodes, e.g., according to EP 1356496.

There are known methods of preparation of oxide protective or abrasion-resistant layers using a low-voltage arc. In a reactive atmosphere, the surface of the cathode is poisoned by oxygen, resulting in reduction of its surface conductivity. This involves uneven evaporation accompanied by increased production of macroparticles. The number of macroparticles is reduced using the method of low-voltage pulse arc or the method of separation of macroparticles. Such methods are described, for example, in documents WO 2006099760 and US 6736949.

The fundamental problem in achieving a stable and economical process of coating layers with low electrical conductivity, for example oxide, is to prevent poisoning of the cathode, which results in reduced speed of deposition in the PVD methods and also - in the case of the low-voltage arc - increased production of macroparticles, and thus generally overall instability of the process.

The aim of the invention is to achieve a new method of creating protective or functional layers, during which the so-called poisoning of the cathode is prevented.

Summary of the invention

In general, subject matter of the invention consists of application of a thin layer with sufficient electrical conductivity to an electrode, which serves as a working cathode, from which it is evaporated using a low-voltage arc or de-dusted by means of cathode sputtering. The advantage is that the working cathode is coated with an electrically conductive material by an auxiliary coating source during the process of
deposition of the protective and functional layers on the substrates in order to increase the electrical conductivity of the surface of this working cathode.

Specifically this issue is addressed, according to the invention presented, by a method of creating protective and functional layers using the PVD method from a cathode with reduced surface electrical conductivity, by means of application from the working coating source, where the principle is that a material is applied to the substrate, but this material is applied from the working coating source made as a rotating working cathode, and the rotating working cathode is coated during the process from an auxiliary coating source with a material with sufficient electrical conductivity where the coat layer applied to the surface of the rotating working cathode has greater electrical conductivity than the surface of this rotating working cathode that is otherwise created during processes without using the coating of the rotating working cathode from an auxiliary coating source. The advantage is that the auxiliary coating source is modified as a rotating auxiliary cathode. Another advantage is the use of a low-voltage arc or magnetron sputtering to apply the material to the substrate from the rotating working cathode. Another advantage is modification of the rotating auxiliary cathode to be used for coating of the working cathode by means of a low-voltage arc or magnetron sputtering. It is also advantageous to apply the coat from the rotating auxiliary cathode to the rotating working cathode in a different atmosphere than the application of the material from the rotating working cathode to the substrate. As far as the atmosphere is concerned, another advantage is if the layer from the rotating auxiliary cathode is applied to the rotating working cathode in a largely non-reactive atmosphere and if the layer from the rotating working cathode to the substrate is applied in a largely reactive atmosphere. The advantage is that in such cases, the reactive atmosphere can contain oxygen. At any rate, it is advantageous to apply the material from the rotating working cathode to the substrate at a different time than the application of from the rotating auxiliary cathode to the rotating working cathode. Alternatively, it is advantageous to apply the material from the rotating working cathode to the substrate at the same time as the coat from the rotating auxiliary cathode to the rotating working cathode. As far as the material of the electrodes is concerned, an advantage is if the material of the rotating working cathode is Al; a great advantage can be if the material of the rotating working cathode is an Al-Cr alloy, with the content of Cr ranging between 0.01 to 80 % of the atomic weight. An advantage is if
the material of the rotating auxiliary cathode is Cr; a great advantage is if the material of the rotating auxiliary cathode is an alloy containing at least partially one of the following elements: Al, Ti, V, Mn, Fe, Co, Ni, Cu, Zr, Nb, Mo, Ag, Hf, Ta, W, Au.

According to the invention, the method is advantageous particularly in situations where the surface of the evaporated material of this working cathode is poorly conductive as a result of the "poisoning" by the reactive gas or a deposition from the gaseous phase, which results in uneven evaporation or de-dusting of this material. This is usually accompanied by process instabilities and, in the case of arc, it results in increased production of macroparticles with the subsequent increased roughness of the surfaces of the substrates coated. Use of the technology according to the invention leads to a maintained sufficient and even electrical conductivity of this working cathode, which results in the process stability and, in the case of evaporation by a low-voltage arc, in significant elimination of the production of macroparticles.

Brief description of the drawings

Further advantages and features of the invention are evident from the following description of the examples of the embodiments accompanied also by the relevant drawings where an example of the method according to the invention with a two-stage process is apparent from the diagrammatic depiction of the equipment shown on Fig. 1 and Fig. 2, and an example of the method according to the invention with a continuous process is apparent from the diagrammatic depiction of the equipment shown on Figs. 3, 4 and 5.

Detailed description of the invention

A suitable material with sufficient electrical conductivity is applied to a surface of the working cathode with insufficient electrical conductivity, e.g., to a surface poisoned by oxygen, nitrogen, layer containing carbon, etc. by an auxiliary coating source in a sufficiently inert atmosphere. A suitable material includes but is not limited to chromium because it is sufficiently electrically conductive in the metallic
state as well as in partially oxidized state, i.e., in the form of sub-oxides. Application of this layer increases electrical conductivity of the surface, which results in significant stabilization of the burning of the low-voltage arc as well as magnetron sputtering. As far as the terms "sufficiently conductive material" and "sufficiently inert atmosphere" are concerned, such determination of conductivity and atmosphere is to be understood as such that the electrical conductivity and inert atmosphere are sufficient to maintain the deposition process stable and to reduce the occurrence of macroparticles.

Without this step consisting of application of the conductive material, the surface of the working cathode is continuously poisoned during the application from the working cathode, which results in instabilities. For example, the low-voltage arc will subsequently create channels with better conductivity on the surface, between which macroparticles, particularly large macroparticles are emitted in increased measure. The result is a layer deposited on the substrates with high roughness, and the useful life of this working cathode is also significantly reduced. In the case of magnetron sputtering, the working pressure is unstable and the deposition speed is reduced.

The simplest way to create a layer with sufficient electrical conductivity on the working cathode is evaporation of the suitable material using a low-voltage arc or magnetron sputtering from the auxiliary cathode in a sufficiently inert atmosphere and the deposition thereof on the working cathode of the arc evaporation equipment or on the working cathode of the magnetron for magnetron cathodic sputtering.

The technology is primarily designed for application of layers of oxide but it can be used also for other types of layers, e.g., layers containing nitride and carbon, in which the deposition of the poorly conductive polymer carbon layer on the surface of the working cathode causes similar problems.

The advantage of the system with rotating cathodes is that it is possible to apply a layer with sufficient electrical conductivity to other part of the working cathode than the one, from which the material of this working cathode is evaporated on the samples, or the coated products, so the auxiliary source of material for the creation of the layer with sufficient electrical conductivity on the working cathode does not have to be placed in the area between the working cathode and the substrates, products,
samples or tools coated. The coating source can also be placed in a screened chamber with sufficiently inert gas.

The method can be used in two different ways

One of the ways is a two-stage process, which consists of two recurring steps: Within the first step, a layer with sufficient electrical conductivity from the auxiliary coating source is applied to the surface of the working cathode in a sufficiently inert atmosphere. Within the second step, the material of the working cathode is evaporated to the product, sample or substrate coated, using a low-voltage arc or cathodic sputtering, e.g., using a magnetron, in a reactive atmosphere, which gradually poisons the surface of the working cathode. Prior to the creation of the poisoned surface, which is monitored via the parameters of the discharge, e.g., voltage of the arc, pressure of the reactive gas, etc., or set empirically by determining the optimal duration, i.e., the process is interrupted and the first step is repeated before the poisoned surface has been created, i.e., application of the layer with sufficient conductivity to the working cathode.

A specific example of the two-stage process is described in Example 1.

The second way is a continuous process: In this case the two steps are combined. The working cathode as well as the auxiliary coating source are located within one shielding. The inert gas is discharged to the area between the evaporated working cathode and the auxiliary coating source, and the reactive gas to the area of the chamber. In this case it is necessary to ensure that only minimum amount of the reactive gas gets to the area between the working cathode and the auxiliary coating source, which required minimization of the gap between the shielding and the working cathode, in which the arc burns in the reactive atmosphere.

A specific example of the continuous process is described in Example 2.

The main advantage of the continuous process as opposed to the two-stage process is the 2-3 times higher speed of coating and the improved homogeneity of the chemical composition.
The auxiliary coating source and the working cathode can be designed for operation based on a low-voltage arc or magnetron. An advantage is if the shape of the working cathode is cylindrical rotary form. The shape of the cathode of the auxiliary coating source can be cylindrical rotary or planar form.

The following specific examples always illustrate the method according to the invention, which is specifically demonstrated on the Pi300 equipment.

Example 1 - Preparation of the layer (Al,Cr)₂O₃ within the two-stage process

There are two rotating cathodes of the low-voltage arc on the side of the chamber 5. The auxiliary cathode 1 is made of Cr; the working cathode 2 is made of Al. During the coating process itself, the two cathodes take turns in burning. The inlet of both gases here is, by example, at a point 8; the chamber pumping is at a point 9. During the first stage the low-voltage arc is burning on the auxiliary cathode 1 with Cr-based material, and Cr is applied to the working cathode 2 made of Al-based material, in the direction 10., as shown on figure No. 1. Rotary shielding 3 or rotary shielding 4 is always turned in such position as to apply the maximum amount of the evaporated material from the auxiliary cathode 1 to the working cathode 2. The shielding 7 prevents application of the coat from the auxiliary cathode 1 to the substrates 6, or products, samples or tools during this stage of the process.

During the second stage, an arc is burning on the working cathode 2 and the mixed material of the auxiliary cathode 1 and of the working cathode 2 is applied to the substrates 6, as shown on Fig. 2.

Process parameters

- Material of the auxiliary cathode 1 - Cr
- Material of the working cathode 2 - Al
- Arc by the auxiliary cathode 1 - 200 A
- Arc by the working cathode 2 - 200 A
- First stage - 100 seem Ar
- Second stage - 150 seem O₂
- Time of burning of the auxiliary cathode 1 - 30 sec
- Time of burning of the working cathode 2 - 30 sec
- Diameter of the cathodes - 80 mm
- Height of the cathodes - 400 mm
- Pressure - approximately 1 Pa
- Speed of application of the material from the auxiliary cathode 1 to the working cathode 2 during the first stage - 10nm/min.

Example 2 - Preparation of the layer (Al, Cr)₂θ₃ in a continuous process

Example 2a

There are two rotating cathodes modified to create a low-voltage arc on the side of the chamber 5, located within one shielding, as shown on Fig. 3.

The auxiliary cathode 1 is made of Cr-based material; the working cathode 2 is made of Al-based material. During the coating process itself, the two cathodes burn at the same time. Ar is taken in through the inlet 8a; O₂ is taken in through the inlet 8b. Inert gas, Ar, is taken into the area between the cathodes 1 and 2 through the shielding 3a, through the above-mentioned inlet 8a. Evaporation of the auxiliary cathode 1 occurs in a sufficiently inert atmosphere. Evaporation of the working cathode 2 occurs in a mixture of an inert gas, Ar, and a reactive gas, O₂. The advantage of the method according to Example 2 as opposed to the method according to Example 1 is the higher (two to three times higher) rate of growth and improved homogeneity of the chemical composition of the deposited layer.

Process parameters
- Material of the auxiliary cathode 1 - Cr
- Material of the working cathode 2 - Al
- Arc by the auxiliary cathode 1 - 200 A
- Arc by the working cathode 2 - 200 A
- Flow ≈ 100 seem Ar, 150 seem O₂
- Diameter of the cathodes - 80 mm
- Height of the cathodes - 400 mm
- Pressure - approximately 1 Pa
- Speed of application of the material from the working cathode 2 to the auxiliary cathode 1 - 10nm/min

Example 2b

Both cathodes are located on the side of the chamber, by example in the chamber door, and the auxiliary cathode 1, which is located within the shielding flown through by the inert gas, e.g., Ar, the material with sufficient electrical conductivity is evaporated to the working cathode 2 from the side and, at the same time, the mixed material, e.g., Al and Cr, is applied from the working cathode 2, made of e.g., of Al, to the substrates in the reaction chamber, e.g., with O₂ or a mixture of O₂ and Ar. The other parameters are similar to example 2a. The advantage of this configuration is that the above-mentioned shielding on the auxiliary cathode 1 can be created as movable or rotating, and so it is then possible to use this auxiliary cathode 1 in a different step of the process, for example in the application of nitride, as a working cathode together with the original working cathode 2. The above-described configuration is apparent on Fig. 4 and Fig 5. N₂ is let in through the inlet 8b during the application of nitride according to Fig. 5.

All the presented values are indicative. In the case of further development or modifications, e.g., in the case of a different size or material of the electrodes these values may differ significantly.

The material of the auxiliary cathode 1 can also be a different conductive material; the material of the working cathode 2 can also be an Al alloy, e.g., Al-Cr alloy, AlSi alloy, or any other suitable material creating oxides or nitrides, e.g., Zr, Ti, etc.

The currents of the arcs can range between 30 - 600 A.

The technology can be combined also with the technology of pulse arc or magnetron.
The working pressures can differ significantly; for application in an oxide atmosphere the partial pressure of oxygen can range from 0.1 to 10 Pa.

List of reference numbers

- 1 - auxiliary cathode Cr
- 2 - working cathode Al
- 3 - rotary shielding of the auxiliary cathode 1
- 3a - shared shielding of the cathodes 1 and 24 - rotary shielding of the working cathode 2
- 5 - coating chamber
- 6 - coated substrate
- 7 - shielding
- 8 - joint inlet of gases O2 and Ar
- 8a - inlet of Ar
- 8b - inlet of O2 (for figure No. 5 inlet of N2)
- 9 - chamber pumping
- 10 - direction of coating from the auxiliary cathode 1 to the working cathode 2
- 11 - direction of coating from the working cathode 2 to the substrates 6

Industrial applicability

The method according to the invention is applicable for the application of protective or functional coatings on various substrates or products, samples or tools.
CLAIMS

1. The method of creating protective and functional layers using the PVD method from a cathode with reduced surface electrical conductivity by way of application from the working coating source characterized in that the substrate (6) is coated with a material, which is applied from the working coating source designed as a rotating working cathode (2), and the rotating working cathode (2) is coated during the process from the auxiliary coating source with material with sufficient electrical conductivity where the layer of the coating applied to the surface of the rotating working cathode (2) has greater electrical conductivity than the surface of this rotating working cathode (2) created during the processes without coating of the rotating working cathode using the auxiliary coating source.

2. The method according to claim 1 characterized in that the auxiliary coating source is modified as a rotating auxiliary cathode (1).

3. The method according to claims 1 and 2 characterized in that the material is applied to the substrate (6) from the rotating working cathode (2) by way of a low-voltage arc or by way of magnetron sputtering.

4. The method according to claims 1 through 3 characterized in that the rotating auxiliary cathode (1) is modified to coat the working cathode (2) by way of a low-voltage arc or by way of magnetron sputtering.

5. The method according to claims 1 through 4 characterized in that the coating is applied from the rotating auxiliary cathode (1) to the rotating working cathode (2) in an atmosphere different from the atmosphere in which material is applied from the rotating working cathode (2) to the substrate (6).
6. The method according to claims 1 through 5 characterized in that the layer is applied from the rotating auxiliary cathode (1) to the rotating working cathode (2) in a largely non-reactive atmosphere, and the layer from the rotating working cathode (2) is applied to the substrate (6) in a largely reactive atmosphere.

7. The method according to claim 6 characterized in that the reactive atmosphere contains oxygen.

8. The method according to claims 1 through 7 characterized in that the material is applied from the rotating working cathode (2) to the substrate (6) at a different time than the time of application of material from the rotating auxiliary cathode (1) to the rotating working cathode (2).

9. The method according to claims 1 through 7 characterized in that the material is applied from the rotating working cathode (2) to the substrate (6) at the same time as the coating from the rotating auxiliary cathode (1) to the rotating working cathode (2).

10. The method according to claims 1 through 9 characterized in that the material of the rotating working cathode (2) is Al.

11. The method according to claims 1 through 9 characterized in that the material of the rotating working cathode (2) is Al-Cr alloy, with Cr content ranging from 0.01 to 80 % of the atomic weight.

12. The method according to claims 1 through 11 characterized in that the material of the rotating auxiliary cathode (1) is Cr.

13. The method according to claims 1 through 11 characterized in that the material of the rotating auxiliary cathode (1) is an alloy containing at least partially one of the following elements: Al, Ti, V, Mn, Fe, Co, Ni, Cu, Zr, Nb, Mo, Ag, Hf, Ta, W, Au.
AMENDED CLAIMS

1. The method of creating protective and functional layers using the PVD method from a cathode with reduced surface electrical conductivity by way of application from the working coating source where the substrate (6) is coated with a material, which is applied from the working coating source designed as a rotating working cathode (2), and the rotating working cathode (2) is coated during the process from the auxiliary coating source, which is modified as a rotating auxiliary cathode (1), characterized in that the rotating working cathode (2) is coated with material with sufficient electrical conductivity where the-layer-of-the-coating applied to the surface of the rotating working cathode (2) has greater electrical conductivity, than the surface of this rotating working cathode (2) created during the processes without coating of the rotating working cathode using the auxiliary coating source, and where the material is applied to the substrate (6) from the rotating working cathode (2) by way of a low-voltage arc sputtering and the rotating auxiliary cathode (1) is modified to coat the working cathode (2) by way of a low-voltage arc sputtering.

2. The method according to claim 1 characterized in that the coating is applied from the rotating auxiliary cathode (1) to the rotating working cathode (2) in an atmosphere different from the atmosphere in which material is applied from the rotating working cathode (2) to the substrate (6).

3. The method according to claims 1 or 2 characterized in that the layer is applied from the rotating auxiliary cathode (1) to the rotating working cathode (2) in a largely non-reactive atmosphere, and the layer from the rotating working cathode (2) is applied to the substrate (6) in a largely reactive atmosphere.

4. The method according to claim 3 characterized in that the reactive atmosphere contains oxygen.
5. The method according to claims 1 through 4 characterized in that the material is applied from the rotating working cathode (2) to the substrate (6) at a different time than the time of application of material from the rotating auxiliary cathode (1) to the rotating working cathode (2).

6. The method according to claims 1 through 4 characterized in that the material is applied from the rotating working cathode (2) to the substrate (6) at the same time as the coating from the rotating auxiliary cathode (1) to the rotating working cathode (2).

7. The method according to claims 1 through 6 characterized in that the material of the rotating working cathode (2) is Al.

8. The method according to claims 1 through 6 characterized in that the material of the rotating working cathode (2) is Al-Cr alloy, with Cr content ranging from 0.01 to 80 % of the atomic weight.

9. The method according to claims 1 through 8 characterized in that the material of the rotating auxiliary cathode (1) is Cr.

10. The method according to claims 1 through 8 characterized in that the material of the rotating auxiliary cathode (1) is an alloy containing at least partially one of the following elements: Al, Ti, V, M, Fe, Co, Ni, Cu, Zr, Nb, Mo, Ag, Hf, Ta, W, Au.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C23C14/00 C23C14/08

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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**X** Further documents are listed in the continuation of Box C

**X** See patent family annex

- Special categories of cited documents
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Name and mailing address of the ISA:
European Patent Office, P B 5816 Patentaald 2 NL - 2280 HV Rijswijk.
Tel (+31-70) 340-2040.
Fax (+31-70) 340-3016

Authorized officer:

Ekhult, Hans
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