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(54) Titre : PROCÉDE ET DISPOSITIF DESTINES A REVETIR UN SUBSTRAT
(54) Title: METHOD AND DEVICE FOR COATING A SUBSTRATE

(57) **Abrégé/Abstract:**

The invention relates to a method for coating a substrate with a layer of a material, such as a metal, in which a quantity of electrically conductive material is vaporized in a space with a low background pressure and energy is supplied to the material which is to be vaporized in order to vaporize this material. According to the invention, the material which is to be vaporized, while it is being vaporized, is kept floating, without support, in the space and is enclosed in an alternating electromagnetic field, the alternating electromagnetic field being generated with the aid of a high-frequency alternating current. The invention also relates to a device for coating a substrate and to a substrate.



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(54) Title: METHOD AND DEVICE FOR COATING A SUBSTRATE

(57) Abstract: The invention relates to a method for coating a substrate with a layer of a material, such as a metal, in which a quantity of electrically conductive material is vaporized in a space with a low background pressure and energy is supplied to the material which is to be vaporized in order to vaporize this material. According to the invention, the material which is to be vaporized, while it is being vaporized, is kept floating, without support, in the space and is enclosed in an alternating electromagnetic field, the alternating electromagnetic field being generated with the aid of a high-frequency alternating current. The invention also relates to a device for coating a substrate and to a substrate.



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METHOD AND DEVICE FOR COATING A SUBSTRATE

The invention relates to a method for coating a substrate with a layer of a material, such as a metal, in which a quantity of electrically conductive material is vaporized in a space with a low background pressure and energy is supplied to the material which is to be vaporized in order to vaporize this material. The invention also relates to a device for coating a substrate, and to a substrate obtained using the method or device.

The method described above is a known technique for coating substrate with (thin) layers of coating material; the method is usually referred to as physical vapour deposition (PVD). This technique is in widespread use in the electronics and optical industries, in the glass industry and in the manufacture of metal-coated plastic sheets for all kinds of applications. PVD is an attractive coating method because the quality which can be achieved is high and there are no waste products produced.

When using PVD, the coating material firstly has to be converted to the vapour phase. This is achieved by heating the coating material in a chamber in which there is a very low background pressure, known as a vacuum chamber. As a result of the heating, the coating material changes to a vapour until a pressure which is in thermodynamic equilibrium with the hot surface of the coating material where the vapour is formed is reached. This equilibrium vapour pressure is the most important parameter for the transfer rate of the coating material to the substrate on which the vapour is deposited. The equilibrium vapour pressure is dependent on the temperature of the coating material. To achieve a reasonable transfer rate of coating material to the substrate, i.e. a reasonable quantity of coating material which is deposited on the substrate per unit time, the coating material generally has to be heated to high temperatures. These temperatures are often of the order of half the boiling point at atmospheric pressure or sometimes even higher. In practice, the temperatures for metals are between approximately 600°C for zinc and approximately 2200°C for niobium and rhenium. Metals such as tantalum, molybdenum and tungsten require such high temperatures that they are not used for PVD. Metals such as titanium, chromium, nickel, aluminium and the like are rarely used as the material transfer rates are low.

A drawback of using PVD is that the transfer rates are limited primarily by the fact that the coating materials which have to be vaporized are always in the liquid state on account of the high process temperatures. Consequently, the material has to be in a crucible, which may be made, for example, from a ceramic material or from copper. In the latter case, intensive cooling with water is required, so that a thin film of solidified coating material covers the copper, with the result that the copper is prevented from melting or being vaporized as well and the copper is not affected. One disadvantageous

consequence of cooling of a copper crucible is that a significant proportion of the heat supplied is lost as a result of the cooling. The use of a ceramic crucible is limited to coating materials which do not enter into a chemical reaction with the crucible material at the high process temperatures. The supply of the thermal energy required also
5 presents a problem when using a ceramic crucible, since most ceramic materials are poor heat conductors.

It is an object of the invention to provide an improved method and device for coating substrates by means of PVD.

Another object of the invention is to provide a method and device of this type in
10 which the transfer rate of the coating material is higher than has hitherto been possible.

Yet another object of the invention is to provide a method and device of this type which in practice make it possible to use materials utilizing PVD as coating material where this has not hitherto been possible.

According to a first aspect of the invention, one or more of these objects are
15 achieved by a method for coating a substrate with a layer of a material, such as a metal, in which a quantity of electrically conductive material is vaporized in a space with a low background pressure and energy is supplied to the material which is to be vaporized in order to vaporize this material, in which method the material which is to be vaporized, while it is being vaporized, is kept floating, without support, in the space
20 and is enclosed in an alternating electromagnetic field, and in which method the alternating electromagnetic field is generated with the aid of a high-frequency alternating current.

Keeping the material which is to be vaporized floating without support in the space means that it is no longer necessary to use a copper or ceramic crucible. As a
25 result, it is possible to impart a higher temperature to the material which is to be vaporized, since the crucible no longer forms the limiting factor. Therefore, the transfer rate of the vaporized material to the substrate can be increased. Since it is no longer necessary to use a crucible, it is also possible to vaporize materials which it has not hitherto been possible to use, on account of their ability to react with the material of the
30 crucible.

It is possible to enclose an electrically conductive material in an alternating electromagnetic field as a result of Lorentz forces, which are generated by the interaction between the external magnetic field and the eddy currents which are thereby induced in the electrically conductive material.

35 The alternating electromagnetic field is generated with the aid of a high-frequency alternating current. A high-frequency alternating current is required so that it is possible to keep floating a sufficiently large mass of electrically conductive material for it to be possible for a quantity of electrically conductive material per minute which

is sufficient for coating of the substrate on an industrial scale to be vaporized efficiently.

The process of floating and melting conducting materials in an alternating electromagnetic field is known under the name "levitation melting". A method and device for this purpose are described in EP 0751361 B1; in this case, the melted material is used for precise casting. It should be noted that a water-cooled crucible, with which the molten material must not come into contact, is still always used. Levitation melting in an alternating electromagnetic field is also described in a number of articles by various authors in "3rd International Symposium on Electromagnetic Processing of Materials, April 3-6 2000, Nagoya, Japan, pp 345-375. Hitherto, however, levitation melting has not been used in conjunction with physical vapour deposition; levitation melting followed by vaporization according to the invention is not known.

The frequency of the alternating current is preferably 10 kHz or higher, more preferably 50 kHz or higher, even more preferably 250 kHz or higher, yet more preferably 1 MHz or higher, and still more preferably 1.5 MHz or higher. The level of the frequency is related to the quantity of material which is to be vaporized per unit time, for example if a substrate is to be coated continuously. This requires a certain vaporizing surface area at a selected temperature of the floating material. This quantity of floating material requires a minimum eddy current in the surface layer of the floating material and therefore a minimum frequency of the alternating current.

According to a preferred embodiment, the alternating electromagnetic field is generated with the aid of an alternating current passing through a coil with a current intensity of 200 A or more, preferably with a current intensity of 500 A or more, more preferably with a current intensity of 1 kA or more, and even more preferably with a current intensity of 4 kA or more. The intensity of the alternating current must be selected as a function of the level of the frequency of the alternating current in order to obtain a sufficient heating capacity.

Preferably, the power which is dissipated in the floating material is at least 2 kW, preferably at least 5 kW, and more preferably at least 10 kW. This is desirable because the vaporization of the floating material increases as the dissipated power becomes greater.

According to an advantageous embodiment of the method, the material which is to be vaporized is heated with the aid of electromagnetic induction heating. In this way, the material which is to be vaporized can be heated to the desired high temperature.

As an alternative or in addition, the material which is to be vaporized can be heated with the aid of laser beams and/or electron bombardment and/or an inductively

coupled plasma and/or resistance heating. All these methods of heating can readily be employed to heat floating material.

The material which is being vaporized is preferably topped up by the alternating electromagnetic field drawing in additional quantities of material which is to be vaporized over the course of time. The action of the alternating electromagnetic field of drawing in material makes it easy to top up the quantity of material which is to be vaporized, which decreases as a result of the vaporization, continuously or in steps.

According to an advantageous embodiment, the alternating electromagnetic field of the coil is shaped in such a manner that a separate section of the alternating field draws in the material to be vaporized. If the material which is to be vaporized is drawn in in a separate section of the alternating field, the section of the alternating field where the material is being vaporized is not disturbed or is disturbed to a lesser extent.

In this case, the material which is to be drawn in preferably does not float freely in the space. It is then easy for the material which is to be drawn in to be moved to a location in the space from which it is then drawn in by the alternating electromagnetic field.

According to a further advantageous embodiment of the method, the separate section of the alternating field is obtained by means of an auxiliary coil which is separate from the coil. As a result, the operation of drawing in the material which is to be vaporized can be controlled and regulated independently of the vaporization of the material.

The above method is preferably used to vaporize titanium, magnesium, tin, zinc, chromium, nickel or aluminium or a mixture of one of these metals with one or more other materials, including these or other metals, since these are commercially important coating materials. After vaporization, some materials may react with a reactive gas, such as oxygen or nitrogen, with the result that nonconductive oxide or nitrides are formed. This reaction may take place during the vapour phase or immediately after the condensation on the substrate.

According to an advantageous embodiment, the substrate is continuously coated with a layer of material. In many cases, this will mean that a substrate is passed through the vacuum chamber in the form of a strip, and during the residence time of a section of the strip in the chamber sufficient material must be vaporized to coat that section of the strip. Hitherto, this was not possible on account of the low transfer rates; however, with the aid of the method as described above, it is possible to vaporize sufficient material sufficiently quickly and therefore to coat a substrate such as a strip on an industrial scale.

A second aspect of the invention provides a device for coating a substrate with a layer of a material, such as a metal, by vaporization of an electrically conductive

material, comprising a chamber provided with means for producing a low background pressure in the chamber, means for receiving the material to be vaporized, and means for heating the material to be vaporized, in which device, according to the invention, the means for receiving the material to be vaporized comprise a coil which can be used
5 to generate an alternating electromagnetic field in order to enable the material which is to be vaporized to float without support.

The provision of the coil makes it possible to make the material which is to be vaporized float, so that there is no longer any need for a crucible, with the result that the method as described above can be carried out with the aid of this device.

10 The coil is preferably designed to generate the alternating electromagnetic field by means of a high-frequency alternating current. Since the coil makes use of a high-frequency alternating current, an alternating electromagnetic field is formed, in which the Lorentz forces can keep the material which is to be vaporized floating.

According to a preferred embodiment, the means for heating the material
15 comprise an electromagnetic induction coil. Consequently, the material which is to be heated can easily be heated to a high temperature without making contact with the material which is to be heated.

With the coil in the device, it is preferably possible to generate the abovementioned high-frequency alternating currents, and preferably also the above-
20 mentioned intensities of the alternating current.

As an alternative or in addition, the means for heating the material comprise a laser and/or an electron source. These means too can be used to heat the material which is to be vaporized, albeit to a slightly lesser extent.

There are preferably means for isolating the coil from the chamber. Isolating the
25 coil from the vaporization space in the vacuum chamber makes it easy to separate the coil from the material which is to be vaporized and allows very good cooling of the coil without contaminating material entering the vaporization chamber and therefore also reaching the substrate. Also, the coolant cannot cause a short circuit in the chamber. As a result, it is possible to enable the coil to take up a high power and transmit this to the
30 material which is to be vaporized. The isolating means are preferably made from ceramic material, since ceramic is resistant to high temperatures and to coolants. The isolating means comprise, for example, a ceramic tube, since this is easy to produce and to use.

The isolating means for the coil also provides the advantage that conductive
35 material which condenses on the isolating materials as a result of eddy currents which are generated by the coil melts or is vaporized, so that it either returns to the floating material as molten material or is used as vapour to coat the substrate. The isolated coil is therefore self-cleaning.

According to an advantageous embodiment, there are feed means for supplying the material which is to be vaporized in wire form, in order to top up the material which vaporizes during use. The material which is to be vaporized has to be constantly topped up on account of the fact that a section of the material is evaporated per unit time; for
5 this purpose, the feed means must be designed in such a manner that the vacuum chamber remains under a vacuum.

Measuring equipment is preferably arranged in the chamber. This measuring equipment is used to control the process. The measuring equipment is preferably suitable, inter alia, for measuring temperature, for example by means of optical
10 pyrometry.

A third aspect of the invention relates to a substrate provided with a layer of electrically conductive material, produced with the aid of the method as described above and/or the device as described above, in which the electrically conductive material is preferably a metal, more preferably titanium, magnesium, tin, zinc,
15 chromium, nickel or aluminium or a mixture of one of these metals and one or more other materials, including these or other metals.

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**Amended CLAIMS for international application PCT/NL03/00139
of 26 April 2004**

1. Method for coating a substrate with a layer of a material, such as a metal, in
5 which a quantity of electrically conductive material is vaporized in a space with a
low background pressure and energy is supplied to the material which is to be
vaporized in order to vaporize this material, wherein the material which is to be
vaporized, while it is being vaporized, is kept floating, without support, in the
10 space and is enclosed in an alternating electromagnetic field, the alternating
electromagnetic field being generated with the aid of a high-frequency alternating
current, characterized in that the substrate is passed through the space in the form
of a strip and is continuously covered with a layer of material.
2. Method according to Claim 1, in which the frequency of the alternating current is
15 10 kHz or higher, preferably 50 kHz or higher, more preferably 250 kHz or
higher, even more preferably 1 MHz or higher, and still more preferably 1.5 MHz
or higher.
3. Method according to Claim 1 or 2, in which the alternating electromagnetic field
20 is generated with the aid of an alternating current passing through a coil with a
current intensity of 200 A or more, preferably with a current intensity of 500 A or
more, more preferably with a current intensity of 1 kA or more, and even more
preferably with a current intensity of 4 kA or more.
- 25 4. Method according to Claim 1, 2 or 3, in which the power which is dissipated in
the floating material is at least 2 kW, preferably at least 5 kW, and more
preferably at least 10 kW.
5. Method according to Claim 1, 2, 3 or 4, in which the material to be vaporized is
30 heated with the aid of electromagnetic induction heating.
6. Method according to one of the preceding claims, in which the material to be
vaporized is heated with the aid of laser beams and/or electron bombardment
and/or an inductively coupled plasma and/or resistance heating.
- 35 7. Method according to one of the Claims 1-6, in which the material being
vaporized is topped up as a result of the alternating electromagnetic field drawing
in additional quantities of material to be vaporized over the course of time.

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8. Method according to Claim 7, in which the alternating electromagnetic field of the coil is shaped in such a manner that a separate section of the alternating field draws in the material to be vaporized.
- 5
9. Method according to Claim 8, in which the material which is to be drawn in does not flow freely in the space.
- 10
10. Method according to Claim 8 or 9, in which the separate section of the alternating field is obtained by means of an auxiliary coil which is separate from the coil.
11. Method according to one of the preceding claims, in which titanium, magnesium, tin, zinc, chromium, nickel or aluminium or a mixture of one of these metals with one or more other materials including these or other metals is vaporized.
- 15
12. Device for coating a substrate with a layer of a material, such as a metal, by vaporization of an electrically conductive material, comprising a chamber provided with means for producing a low background pressure in the chamber, means for receiving the material to be vaporized, and means for heating the material to be vaporized, the means for receiving the material to be vaporized comprising a coil which can be used to generate an alternating electromagnetic field in order to enable the material which is to be vaporized to float without support, characterized in that there are means for isolating the coil from a vaporization space in the chamber, which isolating means comprise a ceramic tube.
- 20
- 25
13. Device according to Claim 12, in which the coil is designed to generate the alternating electromagnetic field by means of a high-frequency alternating current.
- 30
14. Device according to Claim 12 or 13, in which the means for heating the material comprise an electromagnetic induction coil.
15. Device according to Claim 12, 13, or 14, in which the means for heating the material comprise a laser and/or an electron source.
- 35
16. Device according to any one of the Claims 12 - 15, in which the isolating means are made from ceramic material.

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17. Device according to one of Claims 12-16, in which feed means for supplying the material to be vaporized in wire form are provided, in order to top up the material which is being vaporized during use.
- 5
18. Device according to one of Claims 12-17, in which measuring equipment is arranged in the chamber.
19. Device according to Claim 18, in which the measuring equipment is suitable for measuring temperature.
- 10
20. Device according to one of Claims 12-19, which is suitable for carrying out the method according to one of Claims 1-11.
- 15
21. Substrate provided with a layer of electrically conductive material, produced with the aid of a method according to one of Claims 1-11 and/or the device according to one of Claims 12-20, in which the substrate is a strip and the electrically conductive material is preferably a metal, more preferably titanium, magnesium, tin, zinc, chromium, nickel or aluminium or a mixture of one of these metals and one or more other materials, including these or other metals.
- 20