

(19)



(11)

EP 3 488 030 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
16.12.2020 Bulletin 2020/51

(51) Int Cl.:
C25F 3/16 *(2006.01)* **C25F 5/00** *(2006.01)*
C25F 7/00 *(2006.01)*

(21) Application number: **17734749.9**

(86) International application number:
PCT/EP2017/066768

(22) Date of filing: **05.07.2017**

(87) International publication number:
WO 2018/019532 (01.02.2018 Gazette 2018/05)

(54) METHOD FOR POLISHING CONDUCTIVE METAL SURFACES

VERFAHREN ZUM POLIEREN VON LEITFÄHIGEN METALLOBERFLÄCHEN

PROCÉDÉ POUR POLIR DES SURFACES MÉTALLIQUES CONDUCTRICES

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

(30) Priority: **25.07.2016 EP 16181110**

(43) Date of publication of application:
29.05.2019 Bulletin 2019/22

(73) Proprietor: **Leibniz-Institut für Plasmaforschung
und
Technologie e.V.
17489 Greifswald (DE)**

(72) Inventors:
• **POLAK, Martin
17498 Hinrichshagen OT Hof II (DE)**

- **WELTMANN, Klaus-Dieter
18609 Ostseebad Binz (DE)**
- **IHRKE, Roland
17498 Karrendorf (DE)**
- **FRÖHLICH, Maik
17493 Greifswald (DE)**
- **QUADE, Antje
17094 Rowa (DE)**

(74) Representative: **Schulz Junghans
Patentanwälte PartGmbH
Großbeerenstraße 71
10963 Berlin (DE)**

(56) References cited:
EP-A1- 0 874 068 WO-A1-82/02407
WO-A1-2013/066586 WO-A2-2012/172572
RU-C1- 2 537 346 US-B1- 6 627 064

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 3 488 030 B1

DescriptionField of the invention

5 **[0001]** The present invention relates to an electrochemical polishing process for conductive metal surfaces.

Background of the invention

10 **[0002]** Metal surfaces that have a certain degree of surface roughness tend to appear as dull. Polishing of such surfaces reduces the surface roughness by smoothing microscopic peaks in the metal, thereby creating a smooth surface that does not scatter reflexions and therefore appears shiny.

15 **[0003]** Polishing of metal surfaces is required in various situations ranging from smoothing sharp edges on sheets of steel after cutting, defined removal of surface coatings, polishing pieces of jewellery, reduction of friction and reduction of surface areas to minimize corrosion. These applications all have in common that a smooth and shiny surface is to be achieved, with a defined removal of material. A shiny appearance and a limited, defined removal of material is particularly advantageous in the case of polishing jewellery.

20 **[0004]** Methods for polishing metal surfaces known in the state of the art are mechanical polishing, electropolishing, laser polishing, magneto rheological finishing or plasma polishing.

25 **[0005]** Mechanical polishing is performed with rotating polishing wheels usually made of leather, wood, canvas, felt, paper or wool and the use of a polishing agent. The polishing agent contains a carrier such as oil and an abrasive to perform the polishing, depending on the material to be polished.

30 **[0006]** For electropolishing an electrical current is applied to the object which needs polishing and the object is subsequently immersed in an electrolyte solution. The electrical current in combination with the electrolyte removes tiny amounts of the metal surfaces preferably at areas with microscopic peaks of metal, thereby achieving a smoothing process. The metal surfaces are smooth and shiny as a result of this process. The mean profile roughness (R_a) of metal surfaces can, depending on the R_a of the starting material, be reduced by 50% to around $0.2\ \mu\text{m}$ by electropolishing.

35 **[0007]** Plasma polishing is related to electropolishing, but uses a significantly higher voltage, thereby creating a plasma surrounding the object to be polished, separating it from the electrolyte solution. Plasma polishing commonly uses non-hazardous salt solutions as electrolyte in contrast to electropolishing, where hazardous chemicals such as anorganic acids and/or concentrated salt solutions are commonly used. The mean profile roughness (R_a) of metal surfaces can be reduced by up to 85% to around $0.12\ \mu\text{m}$ by plasma polishing as disclosed in DE10207632 B4.

40 **[0008]** WO 82/02407 A1 discloses a plasma polishing method for metals that uses two different voltages applied to the metal, wherein the voltages are in the range of 5V to 30V.

45 **[0009]** All of the above mentioned methods of polishing have drawbacks. Mechanical polishing is difficult to use for structured metal surfaces or areas with limited accessibility as is common in pieces of jewellery. In addition, this method of polishing is very time-consuming, especially with structured surfaces, and in consequence costly. Furthermore, the loss of material is higher with mechanical polishing as compared to other methods. The latter is especially disadvantageous if metal surfaces of precious metals are polished or surface coatings are to be removed.

50 **[0010]** Although electropolishing is suitable for polishing structured surfaces and it leads to less loss of material than mechanical polishing, the use of hazardous chemicals increases the cost and environmental impact of this method.

55 **[0011]** Plasma polishing is, like electropolishing, suitable for the polishing of structured surfaces, is associated with little loss of material and does not require hazardous chemicals, but requires the use of significantly higher voltages to create plasma. This increases potential hazards for personnel and requires suitable measures of protection, increasing attendant costs. Furthermore, the use of higher voltages also results in a significant increase in the power required for this method compared to electropolishing or mechanical polishing. This adds to the costs of this method.

60 **[0012]** The problem underlying the present invention is to provide a method for polishing conductive metal surfaces, achieving a low mean profile roughness (R_a) without the need of hazardous chemicals, with low power consumption and a short processing time. This problem is solved by the subject-matter of the independent claims.

Description of the invention

65 **[0013]** The inventors surprisingly found that the use of ammonium nitrate and ammonium chloride in high dilution as electrolyte in an electrolytic polishing procedure with a voltage below the threshold for generation of plasma is suitable for solving the problem underlying the present invention. This novel polishing method combines the advantages of electropolishing (no need for power consuming plasma generation) and plasmapolishing (use of non-hazardous chemicals; better reduction of surface roughness, lower processing times). Furthermore, the parameters of the method can be adjusted to specific metals and metal alloys and is therefore suitable for a range of applications from polishing of precious metal surfaces to the defined removal of surface coatings.

[0014] The method of the invention is suitable for the polishing of structured and complexly shaped metal surfaces, is associated with little loss of material, a short processing time and does not use hazardous chemicals. The method of the invention therefore provides the means to polish metal surfaces without issues of safety or environmental impact and thereby decreases the costs of polishing. Furthermore, the metal surfaces polished with the method of the invention have exceptionally shiny and smooth surfaces compared to surfaces prepared by mechanical polishing.

[0015] According to a first aspect of the invention a method for polishing conductive metal surfaces is provided. The method comprises the following steps:

- a) providing an electrolyte comprising ammonium nitrate and ammonium chloride, wherein the electrolyte is an aqueous solution comprising 1 to 20 weight percent (wt%) of a mixture of ammonium nitrate and ammonium chloride,
- b) connecting a first electrode to said conductive metal surface and connecting a second electrode to said electrolyte, wherein said conductive metal surface is the anode, then
- c) applying a first electrical voltage to said first electrode and said second electrode in a first voltage step, then
- d) contacting said conductive metal surface with said electrolyte, in an immersion step, then
- e) applying without interruption a second electrical voltage, wherein the first voltage is essentially the same as the second voltage, wherein said second electrical voltage is below the threshold for generating a plasma and between 80 V and 350 V, and
- f) maintaining said second electrical voltage for a period of at least 1 second.

[0016] In other words, the method provided is an electro-chemical polishing method, wherein a conductive metal surface is used as an anode. A second electrode (cathode) is immersed in or conductively connected to the electrolyte. A first electrical voltage is applied between the first and the second electrode either before or after immersion of the anode into the electrolyte. A second electrical voltage is applied between the first and the second electrode without interruption of the flow of an electrical current. Any significant interruption of the flow of an electrical current could negatively affect the outcome of the polishing procedure. The second electrical voltage is below the threshold for the generation of plasma. The generation of plasma at this point prevents the method of the invention to be exercised and it is therefore essential to choose conditions, in particular the second electrical voltage, that prevent the generation of a plasma at this point. A DC voltage between 80 V and 350 V is suitable to exercise the invention. The electric field intensity is higher in the peak areas of the metal surface. This results in a higher removal of material in these areas than in non-peak areas, and thereby creates a smooth surface. Without wishing to be bound by theory, the inventors believe that chemical compounds such as nitrosyl chloride and chloride are generated from the electrolyte, in particular within the gas phase, which contribute to the polishing process.

[0017] In the context of the present specification, the term *metal* also includes metal alloys, whereby an alloy is in the context of the present specification a mixture of two or more elements in which at least one component is a metal.

[0018] According to another embodiment of the invention the method for polishing conductive metal surfaces comprises the additional steps of:

- a) The conductive metal surface is the anode. The second electrode is the cathode. The cathode is electrically connected to or immersed in the electrolyte.
- b) A gas phase surrounding the conductive metal surface is generated comprising the following steps:
 - A first voltage step. This step comprises applying a first electrical DC voltage to the first and the second electrode suitable for the generation of a gas phase followed by an
 - An immersion step. This step comprises contacting the conductive metal surface with the electrolyte.

[0019] In other words, the method provided is an electro-chemical polishing method, wherein the conductive metal surface is used as an anode and is immersed in the electrolyte. The second electrode (cathode) is immersed in or conductively connected to the electrolyte. A gas phase surrounding the conductive metal surface may be generated by applying the first electrical voltage. Once the gas phase is established the second electrical voltage is applied without interruption of the flow of an electrical current. Any significant interruption of the flow of an electrical current would diminish or even completely remove the gas phase. The second electrical voltage is below the threshold for the generation of plasma. The generation of plasma at this point prevents the method of the invention to be exercised and it is therefore essential to choose conditions, in particular the second electrical voltage, that prevent the generation of a plasma at this point. The electric field intensity is higher in the peak areas of the metal surface. This results in a higher removal of material in these areas than in non-peak areas, and thereby creates a smooth surface. Without wishing to be bound by theory, the inventors believe that chemical compounds such as nitrosyl chloride and chloride are generated from the electrolyte, in particular within the gas phase, which contribute to the polishing process.

[0020] According to the invention, the first voltage step precedes the immersion step.

[0021] According to the invention, the first voltage is essentially the same as the second voltage.

[0022] In certain embodiments, 2 to 10 weight percent (wt%), particularly 3 to 8 wt% of the electrolyte is a mixture of ammonium nitrate and ammonium chloride in aqueous solution. Weight percent given are in relation to the total weight of the electrolyte (including the water in case of aqueous solutions).

[0023] In certain embodiments, the treatment time is between 1 second and 1200 seconds, in particular 10 seconds to 600 seconds, more particular 30 seconds to 120 seconds. Treatment time refers to the period of time that the conductive material remains submerged in the electrolyte with the electrical current being applied.

[0024] In certain embodiments, the steps c) to f) are repeated at least once. Long treatment times (> 300 sec) may lead to discolouring or spotting of the treated material. In these cases it is advantageous to increase the number of (shorter) treatments instead of longer treatment times.

[0025] In certain embodiments, the mixture of ammonium nitrate and ammonium chloride used in the electrolyte is characterized by a ratio of the weight of ammonium nitrate to the weight of ammonium chloride between 1:1 to 1:5, in particular 1:3.

[0026] In certain embodiments, the mixture of ammonium nitrate and ammonium chloride used in the electrolyte is characterized by a ratio of ammonium nitrate to ammonium chloride of 1:1. In certain embodiments, the mixture of ammonium nitrate and ammonium chloride used in the electrolyte is characterized by a ratio of ammonium nitrate to ammonium chloride of 1:3. In certain embodiments, the mixture of ammonium nitrate and ammonium chloride used in the electrolyte is characterized by a ratio of ammonium nitrate to ammonium chloride of 1:5. In the context of the present specification, the term a *mixture with a ratio of X:Y* refers to the relation of the weights of two substances in a mixture, whereby the first substance makes up X parts of the mixture and the second substances makes up Y parts of the mixture and the mixture comprises in total X+Y parts. In other words, a mixture of 1:3 refers to 1 part of the first substance and 3 parts of the second substance yielding a mixture with 4 parts. For example: 20g of a 1:3 mixture of ammonium nitrate and ammonium chloride contain 5g of ammonium nitrate and 15g of ammonium chloride.

[0027] In certain embodiments, the conductive metal surface is a precious metal surface, in particular gold and platinum.

[0028] In the context of the present specification, the term *gold* also includes alloys of gold such as coloured gold. Common gold alloys are white gold (gold alloyed with nickel, manganese or palladium), red gold (gold alloyed with copper) and yellow gold (gold alloyed with copper and silver).

[0029] In the context of the present specification, the term *platinum* also includes alloys of platinum. Common platinum alloys comprise in addition to platinum one or more of the following elements; Rhodium, Iridium, Palladium, Ruthenium, Gold, Silver, Copper, Nickel, Cobalt, Tungsten, Titanium or Molybdenum.

[0030] In certain embodiments, the conductive metal surface is a surface coating comprising or essentially consisting of titanium aluminium nitride (TiAlN) or aluminium chromium nitride (AlCrN).

[0031] In certain embodiments, the conductive metal surface is copper or a copper alloy, in particular brass or bronze.

[0032] In the context of the present specification, the term *copper alloy* refers to metal alloys, wherein copper is the principal component.

[0033] In the context of the present specification, the term *bronze* refers to certain copper alloys comprising primarily copper. Non-limiting examples of bronze are the following copper alloys that comprise primarily copper and the indicated element(s): tin bronze (up to 25% tin), aluminium bronze (up to 10% aluminium), lead bronze (up to 26% lead), manganese bronze (up to 12% manganese), silicon bronze (1% to 4% silicon), beryllium bronze (up to 3% beryllium), phosphor bronze (up to 0.5% phosphorus) and red brass (5% tin, 5% zinc and 5% lead).

[0034] In the context of the present specification, the term *brass* is used in its meaning known in the art of metallurgy. It refers to copper alloys comprising mainly copper and zinc. An example of brass is CuZn42, which comprises 58% copper and 42% zinc.

[0035] In certain embodiments, the second electrical voltage applied to the first and the second electrode is dependent on the material of the conductive metal surface. In certain embodiments, the conductive metal surface is:

- gold, and the second electrical voltage is between 80 V and 150 V, in particular the second electrical voltage is 100 V,
- platinum, and the second electrical voltage between 250 V and 350 V, in particular the second electrical voltage is 300 V,
- titanium aluminium nitride (TiAlN), and the second electrical voltage is between 270 V and 350 V, in particular the second electrical voltage is 320 V, or
- aluminium chromium nitride (AlCrN), and the second electrical voltage is between 270 V and 350 V, in particular the second electrical voltage is 320 V.

[0036] In certain embodiments, the conductive metal surface is gold and the second electrical voltage applied to the

first and the second electrode is between 80 V and 150 V, in particular the second electrical voltage is 100 V.

[0037] In certain embodiments, the conductive metal surface is platinum and the second electrical voltage applied to the first and the second electrode is between 250 V and 350 V, in particular the second electrical voltage is 300 V.

[0038] In certain embodiments, the conductive metal surface is titanium aluminium nitride (TiAlN) and the second electrical voltage applied to the first and the second electrode is between 300 V and 340 V, in particular the second electrical voltage is 320 V.

[0039] In certain embodiments, the conductive metal surface is aluminium chromium nitride the second electrical voltage applied to the first and the second electrode is between 300 V and 340 V, in particular the second electrical voltage is 320 V.

[0040] In certain embodiments, the conductive metal surface is conditioned to the same temperature as the electrolyte, prior to contacting the conductive metal surface with the electrolyte. Without wishing to be bound by theory the inventors believe that the gas phase surrounding the conductive metal surface is essential for the success of the present invention. Therefore, in case of the first voltage step preceding the immersion step, the speed of lowering the conductive metal surface into the electrolyte is limited in order not to disturb the integrity of the gas phase surrounding the metal surface immersed in the electrolyte. The generation of the gas phase is also dependent on the temperature of the material that is to be treated. By pre-warming the conductive metal surface, the speed of lowering the conductive metal surface into the electrolyte can be increased without disturbing the integrity of the gas phase. By using a low speed for lowering the conductive metal surface, an uneven loss of material can occur due to differences in treatment time for different parts of the conductive metal surface. Another factor influencing the speed of lowering the conductive metal surface into the electrolyte is the shape of the conductive metal surface.

[0041] In certain embodiments, the speed of lowering the conductive metal surface into the electrolyte is in the range of 0.5 cm/s to 2 cm/s.

[0042] In certain embodiments, the mean profile roughness (R_a) of the conductive metal surface is reduced below 0.03 μm , in particular below 0.02 μm , more particular below 0.01 μm . Methods for measuring R_a known in the art include, without being limited to, atomic force microscopy or a profilometry.

[0043] In the context of the present specification, the term *mean profile roughness* (R_a) refers to a profile roughness parameter. R_a is the arithmetic average of absolute roughness values from a raw profile data of a given surface. It therefore provides the average distance of a point on a surface to the average of the heights and recesses of a surface.

[0044] In certain embodiments, the pH of the electrolyte is between 4.5 to 7.5, in particular 5.5 to 7, more particular 6 to 6.5, most particular 6.1.

[0045] In certain embodiments, the electrical current flowing from the first electrode through the conductive metal surface and the electrolyte to the second electrode by applying the second electrical voltage is between 0.05 A/cm² and 2 A/cm², in particular between 0.1 A/cm² and 1.5 A/cm².

[0046] In certain embodiments, the temperature of the electrolyte is adjusted to a temperature of 40°C to 95°C, in particular to 50°C to 70°C, more particular to 55°C to 65°C.

[0047] In certain embodiments, the metal surface is a precious metal surface and the temperature of the electrolyte is adjusted to a temperature of 50°C to 80°C, in particular 50°C to 60°C.

[0048] In certain embodiments, the metal surface is a titanium aluminium nitride (TiAlN) surface and the temperature of the electrolyte is adjusted to a temperature of 80°C to 95°C.

[0049] In certain embodiments, the metal surface is an aluminium chromium nitride surface and the temperature of the electrolyte is adjusted to a temperature of 80°C to 95°C.

[0050] In certain embodiments, the electrolyte is circulated throughout the duration of the method to avoid localized changes in electrolyte concentration, in particular in the vicinity of the electrodes.

[0051] In certain embodiments, the concentration of the electrolyte is monitored by measuring the conductivity of the electrolyte. In certain embodiments, concentrated electrolyte solution is added during one of the steps of the method of the invention to maintain a constant electrolyte concentration.

[0052] The invention is further illustrated by the following examples, from which further embodiments and advantages can be drawn. These examples are meant to demonstrate the invention, but not to limit its scope.

Examples

[0053] The method of the present invention can be used to polish the conductive surface of various metals, metal alloys and conductive surface coatings.

Polishing of yellow gold surfaces

[0054] The method of the present invention can be used to polish the surface of precious metals such as gold. The treatment of gold surfaces leads to a significant reduction in the roughness of the surface and in consequence to a shiny

appearance as exemplified in the following example.

[0055] The roughness of the gold surface was measured by atomic force microscopy before start of the treatment. The mean profile roughness (R_a) before treatment was 221 nm and the root mean squared roughness (R_q) was 282 nm. Surface roughness was quantified with a scanning probe microscope diCP-II (Veeco) in the "non-contact mode" using a cantilever MPP-11123-10 (Veeco). The surface area measured was $5 \times 5 \mu\text{m}$.

[0056] An aqueous solution with 4 wt% of an ammonium nitrate and ammonium chloride mixture with a ratio of 1:3 was used as electrolyte and pre-warmed to a temperature of 58.8°C prior to the procedure. A first electrode was connected to the gold material, being the anode, and a second electrode being conductively connected to the first electrode was immersed in the electrolyte. A voltage of 100 V DC was applied and the anode (gold material) was lowered into the pre-warmed electrolyte. Upon contact of the gold material with the electrolyte a vapour phase surrounding the gold material was established without occurrence of plasma in the gas phase. The absence of plasma was visually verified by the inventors. The gold material was fully submerged in the electrolyte and the duration of treatment was set at 60 seconds. On the end of the treatment time, power was switched off and the gold material was recovered from the electrolyte and cleaned with water.

[0057] As a result of the polishing method of the present invention the mean profile roughness (R_a) of the gold material was reduced to 12 nm and the root mean squared roughness (R_q) was reduced to 14 nm. Surface roughness was quantified with a scanning probe microscope diCP-II (Veeco) in the "non-contact mode" using a cantilever MPP-11123-10 (Veeco). The surface area measured was $5 \times 5 \mu\text{m}$.

[0058] Further conditions suitable for the method of the present invention are provided in table 1. The electrolyte used was in all examples an aqueous solution with 4 wt% of an ammonium nitrate and ammonium chloride mixture with a ratio of 1:3. The electrolyte was pre-warmed to the temperature indicated. The voltage and current applied as well as the duration of the treatment is provided in table 1.

Table 1: Polishing of yellow gold

Temperature [$^\circ\text{C}$]	Voltage [V]	Current [A]	Duration [s]	Result [+++ polished and shiny; ++ polished; + weakly polished; - not polished]
85	450	0,6	240	- [plasma visible; not suitable]
85	300	1,8	240	- [not suitable]
57	300	4,2	60	- [not suitable]
72	200	10	120	+
70	150	13	120	++
90	150	4	60	++
52,4	100	22	120	+++
58,8	100	15	60	+++
62,1	100	33	120	+++
70,5	100	10	120	+++
82	100	4	120	+++

Polishing of other gold alloy surfaces

[0059] Further gold alloys have been tested in addition to the above mentioned example for the conductive metal surface being yellow gold. The electrolyte used for all tested gold alloys was an aqueous solution with 4 wt% of an ammonium nitrate and ammonium chloride mixture with a ratio of 1:3. The method was performed at different temperatures and the electrolyte was pre-warmed to the according temperature provided in tables 2 and 3.

[0060] The respective gold alloy material was connected to the first electrode and a voltage between 100 V and 300 V DC was applied with the gold alloy being the anode and the cathode being in contact with the electrolyte. The gold alloy material was lowered into the pre-warmed electrolyte. Upon contact of the gold alloy material with the electrolyte a vapour phase surrounding the gold alloy material was established without occurrence of plasma in the gas phase. The absence of plasma was visually verified by the inventors. The gold alloy material was then fully submerged in the electrolyte and the duration of treatment was set as indicated in tables 2 and 3. On the end of the treatment time, power was switched off, the gold alloy material was recovered from the electrolyte, cleaned with water and the polishing effect was graded as indicated in tables 2 and 3.

Table 2: Polishing of gold alloys (red gold)

Temperature [°C]	Voltage [V]	Current [A]	Duration [s]	Result [+++ polished and shiny; ++ polished; + weakly polished; - not polished]
60	300	3	60s	- [not suitable]
57	100	18	40	+++
57	100	16	60	+++
70	100	9	60	++
75	100	9	60	+
76	100	25	5	+

Table 3: Polishing of gold alloys (white gold)

Temperature [°C]	Voltage [V]	Current [A]	Duration [s]	Result [+++ polished and shiny; ++ polished; + weakly polished; - not polished]
57	100	5	30	+++
57	100	5	4x 30	+++
56	100	18	30	+++
57	100	6	300	+++

Polishing of platinum surfaces

[0061] In order to verify the suitability of the method of the present invention for polishing of platinum surfaces an aqueous solution with 4 wt% of an ammonium nitrate and ammonium chloride mixture with a ratio of 1:3 was used. Different temperatures for this method were tested and the electrolyte was pre-warmed to the according temperatures provided in table 4.

[0062] The platinum material was conductively connected to the first electrode and a voltage between 100 V and 350 V DC was applied with the platinum material being the anode and the cathode (second electrode) being in contact with the electrolyte. The platinum surface was lowered into the pre-warmed electrolyte and upon contact with the electrolyte a vapour phase surrounding the anode was established without occurrence of plasma in the gas phase. The absence of plasma was visually verified by the inventors. The platinum material was fully submerged in the electrolyte and the duration of treatment was set as indicated in table 4. On the end of the treatment time, power was switched off, the platinum material was recovered from the electrolyte, cleaned with water and the polishing effect was graded as indicated in table 4.

Table 4: Polishing of platinum

Temperature [°C]	Voltage [V]	Current [A]	Duration [s]	Result [+++ polished and shiny; ++ polished; + weakly polished; - not polished]
57	350	3	60	+
60	300	3	300	+++
62	300	3	600	+++
62	300	3	2x600	+++
58	250	3	300	++
59	150	4	60	+
59	100	6	60	+

Removal of surface coatings

[0063] In addition to the above mentioned materials the method of the invention can also be used to remove surface coatings, in particular surface coatings of tools. The advantage of the present invention in this context is that the surface coating can be specifically removed without material loss of the tool underneath the coating. As a proof of concept two commonly used types of surface coatings, titanium aluminium nitride (TiAlN) and aluminium chromium nitride (AlCrN), were removed from twist drill bits.

[0064] The electrolyte used in this experiment for polishing surface coatings of twist drill bits was an aqueous solution with 4 wt% of an ammonium nitrate and ammonium chloride mixture with a ratio of 1:3. The electrolyte was pre-warmed to the temperature indicated in tables 5 and 6.

[0065] The twist drill bit was connected to the first electrode and a voltage of 320 V DC was applied with the surface coating of the twist drill bit to be polished being the anode and the cathode (second electrode) being in contact with the electrolyte. The material was lowered into the pre-warmed electrolyte. Upon contact of the anode with the electrolyte a vapour phase surrounding the twist drill bit was established without occurrence of plasma in the gas phase. The absence of plasma was visually verified by the inventors. The twist drill bit was fully submerged in the electrolyte and the duration of treatment was set as indicated in tables 5 and 6. On the end of the treatment time, power was switched off, the twist drill bit was recovered from the electrolyte, cleaned with water and the polishing effect was graded as indicated in tables 5 and 6.

Table 5: Polishing of surface coatings (TiAlN)

Temperature [°C]	Voltage [V]	Current [A]	Duration [s]	Result [++ coating removed entirely; + coating removed n parts; - not polished]
87	320	0.6	30	++
90	320	0.6	300	++
90	320	1.9	600	++
90	320	0.6	600	++

Table 6: Polishing of surface coatings (AlCrN)

Temperature [°C]	Voltage [V]	Current [A]	Duration [s]	Result [++ coating removed entirely; + coating removed n parts; - not polished]
87	320	0.6	30	-
90	320	0.4	30	-
90	320	0.6	300	-
90	320	0.6	600	-
90	320	1.6	30 + 600	+
90	320	1.6	30 + 600 + 600	++

Deburring of edges and spikes

[0066] Furthermore, the method of the invention can be used for deburring edges and spikes from all of the above mentioned materials. The advantage of the present invention is that only a minimal and defined amount of material is removed and the surface topology almost remains, apart from the removed sharp edges and spikes that are artefacts of the production process, intact.

[0067] The electrolyte used for deburring edges and spikes of a workpiece was an aqueous solution with 4 wt% of an ammonium nitrate and ammonium chloride mixture with a ratio of 1:3. The electrolyte was pre-warmed to the temperature indicated in table 7.

[0068] The workpiece was connected to the first electrode and a voltage of 320 V DC was applied with the workpiece being the anode and the cathode (second electrode) being in contact with the electrolyte. The workpiece was lowered into the pre-warmed electrolyte and upon contact with the electrolyte a vapour phase surrounding the material was established without occurrence of plasma in the gas phase. The absence of plasma was visually verified by the inventors.

The workpiece was fully submerged in the electrolyte and the duration of treatment was set as indicated in table 7. On the end of the treatment time, the power was switched off and the workpiece was recovered from the electrolyte and cleaned with water. The efficiency of deburring was graded as shown in table 7.

Table 7: Deburring of edges and spikes

Temperature [°C]	Voltage [V]	Current [A]	Duration [s]	Result[++ edges and spikes removed entirely; + edges and spikes removed n parts; - not deburred
87	320	0.6	1	-
90	320	0.4	3	-
90	320	1,6	5	+
90	320	1.6	10	+
90	320	1.6	10	++
90	320	1.6	10	++

Summary

[0069] A method for polishing a conductive metal surface is provided. The method comprises the steps of a) providing an electrolyte comprising ammonium nitrate and ammonium chloride, b) connecting a first electrode to the conductive metal surface and connecting a second electrode to the electrolyte, wherein said conductive metal surface is the anode. Then, a gas phase surrounding the conductive metal surface is generated. This step comprises in no particular order a first voltage step and an immersion step. The first voltage step comprises applying a first electrical voltage to the first and second electrode, wherein this first electrical voltage is suitable for generating the gas phase. The immersion step comprises contacting the conductive metal surface with the electrolyte. Then, a second electrical voltage is applied and maintained for a period of at least 1 second.

Claims

1. A method for polishing a conductive metal surface comprising the steps of

- a) providing an electrolyte comprising ammonium nitrate and ammonium chloride, wherein the electrolyte is an aqueous solution comprising 1 to 20 weight percent (wt%) of a mixture of ammonium nitrate and ammonium chloride,
- b) connecting a first electrode to said conductive metal surface and connecting a second electrode to said electrolyte, wherein said conductive metal surface is the anode, then
- c) applying a first electrical voltage to said first electrode and said second electrode in a first voltage step, then
- d) contacting said conductive metal surface with said electrolyte, in an immersion step, then
- e) applying without interruption a second electrical voltage, wherein the first voltage is essentially the same as the second voltage, wherein said second electrical voltage is below the threshold for generating a plasma and between 80 V and 350 V, and
- f) maintaining said second electrical voltage for a period of at least 1 second.

2. The method according to claim 1, wherein the electrolyte comprises 2 to 10 wt% of a mixture of ammonium nitrate and ammonium chloride.

3. The method according to claim 2, wherein the electrolyte comprises 3 to 8 wt% of a mixture of ammonium nitrate and ammonium chloride.

4. The method according to any one of the preceding claims, wherein ammonium nitrate and ammonium chloride used in the electrolyte is a mixture **characterized by** a ratio of the weight of ammonium nitrate to the weight of ammonium chloride between 1:1 to 1:5, in particular 1:3.

5. The method according to any one of the preceding claims, wherein the conductive metal surface is selected from:

- a precious metal surface, in particular selected from gold and platinum, or
- a surface coating comprising or consisting of titanium aluminium nitride (TiAlN) or aluminium chromium nitride (AlCrN), or
- copper or a copper alloy.

6. The method according to any one of the preceding claims, wherein said conductive metal surface is:

- gold, and the second electrical voltage is between 80 V and 150 V, in particular the second electrical voltage is 100 V,
- platinum, and the second electrical voltage is between 250 V and 350 V, in particular the second electrical voltage is 300 V,
- titanium aluminium nitride (TiAlN), and the second electrical voltage is between 270 V and 350 V, in particular the second electrical voltage is 320 V, or
- aluminium chromium nitride (AlCrN), and the second electrical voltage is between 270 V and 350 V, in particular the second electrical voltage is 320 V.

7. The method according to any one of the preceding claims, wherein the electrolyte has a temperature of 40°C to 95°C.

8. The method according to any one of the preceding claims, wherein a mean profile roughness (R_a) of said conductive metal surfaces is reduced below 0.03 μm , in particular below 0.02 μm , more particular below 0.01 μm .

9. The method according to any one of the preceding claims, wherein a pH of the electrolyte is between 4.5 to 7.5, particular wherein the pH is 6.1.

10. The method according to any one of the preceding claims, wherein an electrical current by applying the second electrical voltage is between 0.05 A/cm² and 2 A/cm², in particular between 0.1 A/cm² and 1.5 A/cm².

11. The method according to claim 7, wherein the conductive metal surface is conditioned to the temperature of said electrolyte, prior to contacting said conductive metal surface with said electrolyte.

Patentansprüche

1. Verfahren zum Polieren einer leitfähigen Metalloberfläche, umfassend die folgenden Schritte:

- a) Bereitstellen eines Elektrolyten umfassend Ammoniumnitrat und Ammoniumchlorid, wobei der Elektrolyt eine wässrige Lösung ist, die 1 bis 20 Gewichtsprozent (Gew.-%) einer Mischung aus Ammoniumnitrat und Ammoniumchlorid umfasst,
- b) Verbinden einer ersten Elektrode mit der leitfähigen Metalloberfläche und Verbinden einer zweiten Elektrode mit dem Elektrolyten, wobei die leitfähige Metalloberfläche die Anode ist, dann
- c) Anlegen einer ersten elektrischen Spannung an die erste Elektrode und die zweite Elektrode in einem ersten Spannungsschritt, dann
- d) Kontaktieren der leitfähigen Metalloberfläche mit dem Elektrolyten in einem Eintauchschritt, dann
- e) unterbrechungsfreies Anlegen einer zweiten elektrischen Spannung, wobei die erste Spannung im Wesentlichen die gleiche wie die zweite Spannung ist, wobei die zweite elektrische Spannung unter dem Grenzwert zum Erzeugen eines Plasmas liegt und zwischen 80 V und 350 V beträgt, und
- f) Beibehalten der zweiten elektrischen Spannung über eine Zeitdauer von mindestens 1 Sekunde.

2. Verfahren nach Anspruch 1, wobei der Elektrolyt zu 2 bis 10 Gew.-% einer Mischung aus Ammoniumnitrat und Ammoniumchlorid umfasst.

3. Verfahren nach Anspruch 2, wobei der Elektrolyt zu 3 bis 8 Gew.-% einer Mischung aus Ammoniumnitrat und Ammoniumchlorid umfasst.

4. Verfahren nach einem der vorhergehenden Ansprüche, wobei das in dem Elektrolyten verwendete Ammoniumnitrat und Ammoniumchlorid eine Mischung ist, die durch ein Verhältnis des Ammoniumnitratsgewichts zu dem Ammoniumchloridgewicht von 1:1 bis 1:5, insbesondere 1:3, gekennzeichnet ist.

5. Verfahren nach einem der vorhergehenden Ansprüche, wobei die leitfähige Metalloberfläche aus Folgendem ausgewählt ist:

- einer Edelmetalloberfläche, die insbesondere aus Gold und Platin ausgewählt ist, oder
- einer Oberflächenbeschichtung, die Titan-Aluminiumnitrid (TiAlN) oder Aluminium-Chromnitrid umfasst oder daraus besteht, oder
- Kupfer oder einer Kupferlegierung.

6. Verfahren nach einem der vorhergehenden Ansprüche, wobei die leitfähige Metalloberfläche Folgendes ist:

- Gold und die zweite elektrische Spannung zwischen 80 V und 150 V beträgt, wobei die zweite elektrische Spannung insbesondere 100 V beträgt,
- Platin und die zweite elektrische Spannung zwischen 250 V und 350 V beträgt, wobei die zweite elektrische Spannung insbesondere 300 V beträgt,
- Titan-Aluminiumnitrid (TiAlN) und die zweite elektrische Spannung zwischen 270 V und 350 V beträgt, wobei die zweite elektrische Spannung insbesondere 320 V beträgt, oder
- Aluminium-Chromnitrid und die zweite elektrische Spannung zwischen 270 V und 350 V beträgt, wobei die zweite elektrische Spannung insbesondere 320 V beträgt.

7. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Elektrolyt eine Temperatur von 40 °C bis 95 °C aufweist.

8. Verfahren nach einem der vorhergehenden Ansprüche, wobei ein Mittenrauwert (R_a) der leitfähigen Metalloberflächen unter 0,03 μm verringert wird, insbesondere unter 0,02 μm , genauer insbesondere unter 0,01 μm .

9. Verfahren nach einem der vorhergehenden Ansprüche, wobei ein pH-Wert des Elektrolyten zwischen 4,5 und 7,5 beträgt, insbesondere wobei der pH-Wert 6,1 beträgt.

10. Verfahren nach einem der vorhergehenden Ansprüche, wobei ein elektrischer Strom durch Anlegen der zweiten elektrischen Spannung zwischen 0,05 A/cm² und 2 A/cm² beträgt, insbesondere zwischen 0,1 A/cm² und 1,5 A/cm².

11. Verfahren nach Anspruch 7, wobei die leitfähige Metalloberfläche auf die Temperatur des Elektrolyten angepasst wird, bevor die leitfähige Metalloberfläche mit dem Elektrolyten kontaktiert wird.

Revendications

1. Procédé pour polir une surface métallique conductrice comportant les étapes de

- a) fourniture d'un électrolyte comportant du nitrate d'ammonium et du chlorure d'ammonium, dans lequel l'électrolyte est une solution aqueuse comportant de 1 % en poids à 20 % en poids d'un mélange de nitrate d'ammonium et de chlorure d'ammonium,
- b) connexion d'une première électrode à ladite surface métallique conductrice et connexion d'une seconde électrode audit électrolyte, dans lequel ladite surface métallique conductrice est l'anode, puis
- c) application d'une première tension électrique à ladite première électrode et à ladite seconde électrode dans une première étape de tension, puis
- d) mise en contact de ladite surface métallique conductrice avec ledit électrolyte dans une étape d'immersion, puis
- e) application, sans interruption, d'une seconde tension électrique, dans lequel la première tension est essentiellement la même que la seconde tension, dans lequel ladite seconde tension électrique est inférieure au seuil pour générer un plasma et entre 80 V et 350 V et
- f) maintien de ladite seconde tension électrique pendant une période d'au moins 1 seconde.

2. Procédé selon la revendication 1, dans lequel l'électrolyte comporte de 2 % en poids à 10 % en poids d'un mélange de nitrate d'ammonium et de chlorure d'ammonium.

3. Procédé selon la revendication 2, dans lequel l'électrolyte comporte de 3 % en poids à 8 % en poids d'un mélange de nitrate d'ammonium et de chlorure d'ammonium.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel du nitrate d'ammonium et du chlorure d'ammonium utilisés dans l'électrolyte est un mélange **caractérisé par** un rapport entre le poids de nitrate d'ammonium et le poids de chlorure d'ammonium compris entre 1:1 et 1:5, en particulier 1:3.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel la surface métallique conductrice est sélectionnée parmi :

- une surface en métal précieux, en particulier sélectionné parmi de l'or et du platine ou
- un revêtement de surface comportant du nitrure de titane-aluminium (TiAlN) ou du nitrure d'aluminium-chrome (AlCrN) ou constitué de l'un des deux
- du cuivre ou un alliage de cuivre.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite surface métallique conductrice est :

- de l'or et la seconde tension électrique est comprise entre 80 V et 150 V, en particulier la seconde tension électrique est de 100 V,
- du platine et la seconde tension électrique est comprise entre 250 V et 350 V, en particulier la seconde tension électrique est de 300 V,
- du nitrure de titane-aluminium (TiAlN) et la seconde tension électrique est comprise entre 270 V et 350 V, en particulier la seconde tension électrique est de 320 V ou
- du nitrure d'aluminium-chrome (AlCrN) et la seconde tension électrique est comprise entre 270 V et 350 V, en particulier la seconde tension électrique est de 320 V.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'électrolyte a une température de 40 °C à 95 °C.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel une rugosité de profil moyenne (R_a) desdites surfaces métalliques conductrices est réduite en-dessous de 0,03 μm , en particulier en-dessous de 0,02 μm , plus particulièrement en-dessous de 0,01 μm .

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel un pH de l'électrolyte est compris entre 4,5 et 7,5, en particulier dans lequel le pH est de 6,1.

10. Procédé selon l'une quelconque des revendications précédentes, dans lequel un courant électrique par application de la seconde tension électrique est compris entre 0,05 A/cm² et 2 A/cm², en particulier entre 0,1 A/cm² et 1,5 A/cm².

11. Procédé selon la revendication 7, dans lequel la surface métallique conductrice est conditionnée à la température dudit électrolyte, avant la mise en contact de ladite surface métallique conductrice avec ledit électrolyte.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- DE 10207632 B4 [0007]
- WO 8202407 A1 [0008]