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(54) **ELECTROLYTE AND PROCESS FOR THE ELECTROLYTIC POLISHING OF A METALLIC SUBSTRATE**

(57) The present invention is directed at an electrolyte (EL) for the electrolytic polishing of a metallic substrate comprising at least one acid compound (A), at least one fluoride compound (F), and at least one complexing

agent (CA). Furthermore, the invention is directed at a process for the electrolytic polishing of a metallic substrate wherein the electrolyte (EL) is applied.

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## Description

**[0001]** The shaping and surface finishing of metallic substrates has often proven a challenge. In particular the shaping and surface finishing of metallic substrates obtained from generative processes such as additive layer manufacturing often exhibit rough surfaces. The commonly known shaping and surface finishing methods such as abrasive flow machining are often not applicable to complex surfaces. Furthermore, electrochemical methods are known, such as electrolytic polishing. The electrolytic polishing effect relies on a dissolution reaction occurring on a metallic substrate forming part of an electrolytic cell when a current is applied, wherein the metallic substrate is dissolved into the electrolyte in form of ions. Without wishing to be bound to by a theory, it is believed that an electrolytic film is formed on the surface of the metallic substrate and due to the difference in surface ratio and discharge behaviour peaks are dissolved more rapidly than plane surfaces resulting in a reduction of surface roughness. However, state of the art electrolytic polishing processes are often cost and time intensive or do not result in the desired reduction of surface roughness. Furthermore, it is often required to apply hazardous chemicals which require a cumbersome disposal. Thus, it is an object of the present invention to provide an electrolytic polishing process which does not suffer from the drawbacks indicated above.

**[0002]** The finding of the present invention is an electrolyte (EL) for the application in an electrolytic polishing process for metallic substrates, resulting in an excellent reduction of surface roughness.

**[0003]** In a first aspect the invention is directed at an electrolyte (EL) for the electrolytic polishing of a metallic substrate comprising

- (i) at least one acid compound (A),
- (ii) at least one fluoride compound (F), and
- (iii) at least one complexing agent (CA).

**[0004]** In an embodiment the electrolyte (EL) comprises

- (i) the at least one acid compound (A) in an amount of not more than 20 wt.-%, preferably in an amount of not more than 15 wt.-%, more preferably in an amount of not more than 10 wt.-%, even more preferably in an amount of not more than 5 wt.-%, like an amount in the range of 0.05 to 20 wt.-%, preferably an amount in the range of 0.5 to 15 wt.-%, more preferably an amount in the range of 1 to 10 wt.-%, even more preferably an amount in the range of 1 to 5 wt.-%, based on the weight of the electrolyte (EL), and/or
- (ii) the at least one fluoride compound (F) in an amount of not more than 40 wt.-%, preferably in an amount of not more than 30 wt.-%, more preferably in an amount of not more than 15 wt.-%, even more

preferably in an amount of not more than 10 wt.-%, like an amount in the range of 1 to 40 wt.-%, preferably an amount in the range of 1 to 30 wt.-%, more preferably an amount in the range of 2 to 15 wt.-%, even more preferably an amount in the range of 4 to 10 wt.-%, based on the weight of the electrolyte (EL), and/or

(iii) the at least one complexing agent (CA) in an amount of not more than 30 wt.-%, preferably in an amount of not more than 20 wt.-%, more preferably in an amount of not more than 10 wt.-%, even more preferably in an amount of not more than 5 wt.-%, like an amount in the range of 0.5 to 30 wt.-%, preferably an amount in the range of 0.5 to 20 wt.-%, more preferably an amount in the range of 0.5 to 10 wt.-%, even more preferably an amount in the range of 0.5 to 5 wt.-%, yet even more preferably an amount in the range of 1 to 3 wt.-%, based on the weight of the electrolyte (EL).

**[0005]** In an embodiment the electrolyte (EL) consists of

- (i) at least one acid compound (A),
- (ii) at least one fluoride compound (F),
- (iii) at least one complexing agent (CA),
- (iv) at least one medium (M), and
- (v) optionally additives (AD).

**[0006]** In an embodiment the electrolyte (EL) comprises

- (i) the at least one acid compound (A) in an amount of not more than 20 wt.-%, preferably in an amount of not more than 15 wt.-%, more preferably in an amount of not more than 10 wt.-%, even more preferably in an amount of not more than 5 wt.-%, like an amount in the range of in the range of 0.05 to 20 wt.-%, preferably an amount in the range of 0.5 to 15 wt.-%, more preferably an amount in the range of 1 to 10 wt.-%, even more preferably an amount in the range of 1 to 5 wt.-%, based on the weight of the electrolyte (EL), and/or
- (ii) the at least one fluoride compound (F) in an amount of not more than 40 wt.-%, preferably in an amount of not more than 30 wt.-%, more preferably in an amount of not more than 15 wt.-%, even more preferably in an amount of not more than 10 wt.-%, like an amount in the range of 1 to 40 wt.-%, preferably an amount in the range of 1 to 30 wt.-%, more preferably an amount in the range of 2 to 15 wt.-%, even more preferably an amount in the range of 4 to 10 wt.-%, based on the weight of the electrolyte (EL), and/or
- (iii) the at least one complexing agent (CA) in an amount of not more than 30 wt.-%, preferably in an amount of not more than 20 wt.-%, more preferably in an amount of not more than 10 wt.-%, even more

preferably in an amount of not more than 5 wt.-%, like an amount in the range of 0.5 to 30 wt.-%, preferably an amount in the range of 0.5 to 20 wt.-%, more preferably an amount in the range of 0.5 to 10 wt.-%, even more preferably an amount in the range of 0.5 to 5 wt.-%, yet even more preferably an amount in the range of 1 to 3 wt.-%, based on the weight of the electrolyte (EL), and/or

(iv) the at least one medium (M) in an amount of at least 10 wt.-%, preferably in an amount of at least 30 wt.-%, more preferably in an amount of at least 50 wt.-%, even more preferably in an amount of at least 70 wt.-%, like an amount in the range of 10 to 98.5 wt.-%, preferably an amount in the range of 30 to 95 wt.-%, more preferably an amount in the range of 50 to 90 wt.-%, even more preferably an amount in the range of 70 to 85 wt.-%, based on the weight of the electrolyte (EL), and/or

(v) the additives (AD) in an amount of not more than 25 wt.-%, preferably in an amount of not more than 15 wt.-%, more preferably in an amount of not more than 10 wt.-%, even more preferably in an amount of not more than 5 wt.-%, yet even more preferably in an amount of not more than 2 wt.-%, like an amount in the range of 0.01 to 25 wt.-%, preferably an amount in the range of 0.01 to 10 wt.-%, more preferably an amount in the range of 0.01 to 5 wt.-%, even more preferably an amount in the range of 0.01 to 2 wt.-%, based on the weight of the electrolyte (EL).

**[0007]** In an embodiment the at least one acid compound (A) is selected from the group consisting of inorganic or organic acids such as sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, formic acid, acetic acid propionic acid, or mixtures thereof, preferably is selected from the group consisting of sulfuric acid, nitric acid, phosphoric acid, or mixtures thereof, more preferably is sulfuric acid.

**[0008]** In an embodiment the at least one fluoride compound (F) is selected from the group consisting of ammonium fluoride, sodium fluoride, potassium fluoride, magnesium fluoride, calcium fluoride, trifluoroacetic acid, or mixtures thereof, preferably is selected from the group consisting of ammonium fluoride, sodium fluoride, potassium fluoride, magnesium fluoride, calcium fluoride, or mixtures thereof, more preferably is ammonium fluoride.

**[0009]** In an embodiment the at least one complexing agent (CA) is selected from the group consisting of methylglycindiacytic acid (MGDA), ethylenediaminetetraacetate (EDTA), diethylenetriaminepentakis(methylenephosphonic acid (DTPMP) aminopolycarboxylic acids (APC) diethylenetriaminepentaacetate (DTPA), nitrilotriacetate (NTA), triphosphate, 1,4,7,10 tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA), phosphonate, diethylenetriaminepentakis(methylenephosphonic acid (DTPMP), gluconic acid,  $\beta$ -alaninediacetic acid (ADA), N-bis[2-(1,2 dicarboxy-ethoxy)ethyl]glycine (BCA5), N-bis[2-(1,2-dicarboxyethoxy)ethyl]aspatic acid (BCA6),

tetrakis(2-hydroxypropyl)-ethylenediamine (THPED), N-(Hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA) or mixtures thereof, preferably is selected from the group consisting of methylglycindiacytic acid (MGDA), ethylenediaminetetraacetate (EDTA), diethylenetriaminepentakis(methylenephosphonic acid (DTPMP) aminopolycarboxylic acids (APC) diethylenetriaminepentaacetate (DTPA), diethylenetriaminepentakis(methylenephosphonic acid (DTPMP), tetrakis(2-hydroxypropyl)ethylenediamine (THPED), N-(hydroxyethyl)-ethylenediamine-triacetic acid (HEDTA), or mixtures thereof, more preferably is methylglycindiacytic acid (MGDA).

**[0010]** In a second aspect the present invention is directed at a process for the electrolytic polishing of a metallic substrate comprising the steps of

- (i) providing an electrolyte (EL) as described herein in an electrolytic cell comprising at least one electrode,
- (ii) disposing a metallic substrate as an anode in the electrolytic cell,
- (iii) applying a current from a power source between the at least one electrode and the metallic substrate, and
- (iv) immersing the metallic substrate in the electrolyte (EL).

**[0011]** In an embodiment the current is applied at a voltage of not more than 100 V, preferably of not more than 80 V, more preferably of not more than 50 V, even more preferably of not more than 20 V, like in the range of 1 to 100 V, preferably in the range of 1 to 80 V, more preferably in the range of 1 to 50 V, even more preferably in the range of 1 to 20 V, yet even more preferably in the range of 5 to 20 V.

**[0012]** In an embodiment the electrolyte has a temperature in the range of 10 to 95 °C, preferably a temperature in the range of 40 to 95 °C, more preferably a temperature in the range of 60 to 95 °C, even more preferably a temperature in the range of 70 to 90 °C, yet even more preferably a temperature in the range of 75 to 85 °C.

**[0013]** In an embodiment the current is applied at a current density in the range of 0.05 to 10 A/cm<sup>2</sup>, preferably at a current density in the range of 0.05 to 5 A/cm<sup>2</sup>, more preferably at a current density in the range of 0.1 to 2.5 A/cm<sup>2</sup>, even more preferably at a current density in the range of 0.1 to 2.0 A/cm<sup>2</sup>, yet even more preferably at a current density in the range of 0.1 to 1.5 A/cm<sup>2</sup>.

**[0014]** In an embodiment the current is applied for a time in the range of 1 to 240 min, preferably for a time in the range of 1 to 120 min, more preferably for a time in the range of 1 to 60 min, even preferably for a time in the range of 1 to 30 min, yet even more preferably for a time in the range of 2 to 20 min.

**[0015]** In an embodiment the process comprises at least one additional process step of treating the metallic substrate with a cleaning composition.

**[0016]** In a third aspect the present invention is directed at the use of at least one complexing agent (CA) in an electrolyte to increase the efficiency of surface roughness reduction in an electrolytic polishing process of a metallic substrate.

**[0017]** In a fourth aspect the present invention is directed at the use of at least one complexing agent (CA) in an electrolyte to increase the lifetime of the electrolyte when applied in an electrolytic polishing process of a metallic substrate.

**[0018]** It is to be understood that the different aspects of the invention and the embodiments described above and below are interrelated such that the disclosures supplement each other. For example the electrolyte described according to the first aspect is preferably applied in the process according to the second aspect and the use according to the third and fourth aspect.

**[0019]** In the following the invention is described in more detail:

The invention is directed at an electrolyte (EL) for the electrolytic polishing of a metallic substrate with excellent long-term stability and efficiency of surface roughness reduction when applied in an according process.

## THE ELECTROLYTE (EL)

**[0020]** The invention is directed at an electrolyte (EL). The term "electrolyte" as used according to the present invention is directed at a fluid that can be applied in an electrolytic cell as conducting medium in which the flow of current is accompanied by the movement of matter in the form of ions.

**[0021]** The electrolyte (EL) for the electrolytic polishing of a metallic substrate comprises at least one acid compound (A), at least one fluoride compound (F), and at least one complexing agent (CA).

**[0022]** In a preferred embodiment the electrolyte (EL) does not comprise any other acid compounds, fluoride compounds and complexing agents beside the at least one acid compound (A), the at least one fluoride compound (F), and the at least one complexing agent (CA).

**[0023]** In a preferred embodiment the electrolyte (EL) is acidic. It is appreciated that the electrolyte has a pH of not more than 6.5, preferably a pH of not more than 6.0, more preferably a pH of not more than 5.5, like a pH in the range of 0.5 to 6.5, preferably a pH in the range of 1.0 to 6.0, more preferably a pH in the range of 2.0 to 5.5, even more preferably a pH in the range of 3.0 to 5.0.

## The Acid Compound (A)

**[0024]** The term "acid compound" as used according to the present invention is directed at an organic or inorganic compound that can accept a pair of electrons to form a covalent bond.

**[0025]** The at least one acid compound (A) is an essential constituent of the electrolyte (EL). The at least one acid compound (A) increases the conductivity of the electrolyte and may benefit an electrolytic polishing process as a catalyst depending on the metallic substrate to be treated.

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**[0026]** Preferably the at least one acid compound (A) is comprised in the electrolyte (EL) in an amount of not more than 20 wt.-%, preferably in an amount of not more than 15 wt.-%, more preferably in an amount of not more than 10 wt.-%, even more preferably in an amount of not more than 5 wt.-%, like an amount in the range of in the range of 0.05 to 20 wt.-%, preferably an amount in the range of 0.5 to 15 wt.-%, more preferably an amount in the range of 1 to 10 wt.-%, even more preferably an amount in the range of 1 to 5 wt.-%, based on the weight of the electrolyte (EL).

**[0027]** It is appreciated that the at least one acid compound (A) is selected from the group consisting of inorganic or organic acids such as sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, formic acid, acetic acid propionic acid, or mixtures thereof, preferably is selected from the group consisting of sulfuric acid, nitric acid, phosphoric acid, or mixtures thereof, more preferably is sulfuric acid.

**[0028]** In a preferred embodiment the at least one acid compound (A) is aqueous sulfuric acid, wherein sulfuric acid is comprised in an amount in the range of 100 to 20 wt.-%, preferably in an amount in the range of 98 to 50 wt.-%, more preferably in an amount in the range of 98 to 80 wt.-%, even more preferably in an amount in the range of 98 to 90 wt.-%, based on the weight of the at least one acid compound (A).

**[0029]** Thus, it is not required to include toxic acid compounds requiring cumbersome disposal, such as hydrofluoric acid, which is disclosed as a suitable acid compound for the electrolytic polishing of metallic substrates in the state of the art.

## The Fluoride Compound (F)

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**[0030]** The term "fluoride compound" as used according to the present invention is directed at a compound that can serve as a source of fluoride ions. Depending on the metallic substrate to be treated in an electrolytic polishing process fluoride ions may be required to support the dissolution process, for example by forming stable complexes with dissolved metal ions.

**[0031]** Preferably the at least one fluoride compound (F) is comprised in the electrolyte (EL) in an amount of not more than 40 wt.-%, preferably in an amount of not more than 30 wt.-%, more preferably in an amount of not more than 15 wt.-%, even more preferably in an amount of not more than 10 wt.-%, like an amount of in the range of 1 to 40 wt.-%, preferably an amount in the range of 1 to 30 wt.-%, more preferably in an amount the range of 2 to 15 wt.-%, even more preferably an amount in the range of 4 to 10 wt.-%, based on the weight of the electrolyte (EL). It is appreciated that the at least one fluoride

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compound (F) is selected from the group consisting of ammonium fluoride, sodium fluoride, potassium fluoride, magnesium fluoride, calcium fluoride, trifluoroacetic acid, or mixtures thereof, preferably is selected from the group consisting of ammonium fluoride, sodium fluoride, potassium fluoride, magnesium fluoride, calcium fluoride, or mixtures thereof, more preferably is ammonium fluoride.

**[0032]** It is believed that the application of ammonium fluoride additionally benefits the process of electrolytic polishing of metallic substrates by providing a cationic wetting agent ( $\text{NH}_4^+$ ) which modifies the polarization of the electrodes.

### The Complexing Agent (CA)

**[0033]** The term "complexing agent" as used according to the present invention is directed at compounds that form coordinate bonds with a metal atom or ion. Chelating agents are complexing agents that form a particular type of complex, that involves the formation or presence of two or more separate coordinate bonds between a polydentate (multiple bonded) ligand and a multivalent single central atom. Usually these ligands are organic compounds, and are called chelants, chelators, chelating agents, or sequestering agents. The term "complexing agent" includes both non-chelating complexing agents and chelating complexing agents, the latter being preferred.

**[0034]** The at least one complexing agent (CA) is an essential constituent of the electrolyte (EL). The at least one complexing agent (CA) benefits the long-term stability of the electrolyte (EL) and increases the efficiency of surface roughness reduction achieved by electrolytic polishing of a metallic substrate.

**[0035]** Preferably the at least one complexing agent (CA) is comprised in the electrolyte (EL) in an amount of not more than 30 wt.-%, preferably in an amount of not more than 20 wt.-%, more preferably in an amount of not more than 10 wt.-%, even more preferably in an amount of not more than 5 wt.-%, like an amount in the range of 0.5 to 30 wt.-%, preferably an amount in the range of 0.5 to 20 wt.-%, more preferably an amount in the range of 0.5 to 10 wt.-%, even more preferably an amount in the range of 0.5 to 5 wt.-%, yet even more preferably an amount in the range of 1 to 3 wt.-%, based on the weight of the electrolyte (EL)

**[0036]** It is appreciated that the at least one complexing agent (CA) is selected from the group consisting of methylglycindiactic acid (MGDA), ethylenediaminetetraacetate (EDTA), diethylenetriaminepentakis(methylene)phosphonic acid (DTPMP), aminopolycarboxylic acids (APC), diethylenetriaminepentaacetate (DTPA), nitrilotriacetate (NTA), triphosphate, 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA), phosphonate, diethylenetriaminepentakis(methylene)phosphonic acid (DTPMP), gluconic acid,  $\beta$ -alaninediacetic acid (ADA), N-bis[2-(1,2-dicarboxy-ethoxy)ethyl]glycine (BCA5), N-bis[2-(1,2-dicarboxyethoxy)ethyl]-aspartic acid (BCA6),

tetrakis(2-hydroxypropyl)ethylenediamine (THPED), N-(hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA) or mixtures thereof, preferably is selected from the group consisting of methylglycindiactic acid (MGDA), ethylenediaminetetraacetate (EDTA), diethylenetriamine-pentakis(methylene)phosphonic acid (DTPMP), aminopolycarboxylic acids (APC), diethylenetriaminepentaacetate (DTPA), diethylenetriaminepentakis(methylene)phosphonic acid (DTPMP), tetrakis(2-hydroxypropyl)ethylenediamine (THPED), N-(hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA), or mixtures thereof, more preferably is methylglycindiactic acid (MGDA).

### 15 The Medium (M)

**[0037]** The electrolyte (EL) may comprise at least one medium (M). The term "medium" as used according to the present invention is directed at any organic or inorganic compound suitable for providing a medium wherein the electrolytic polishing of metallic substrates can be conducted. Preferably the at least one medium (M) benefits the process of electrolytic polishing of metallic substrates, for example by increasing the conductivity of the electrolytic cell, by stabilizing the complexes formed by the at least one complexing agent (CA) and/or by providing a sufficient solubility with respect to the compounds comprised in the electrolyte (EL).

**[0038]** Preferably the at least one medium (M) is comprised in the electrolyte (EL) in an amount of at least 10 wt.-%, preferably in an amount of at least 30 wt.-%, more preferably in an amount of at least 50 wt.-%, even more preferably in an amount of at least 70 wt.-%, like an amount in the range of 10 to 98.5 wt.-%, preferably an amount in the range of 30 to 95 wt.-%, more preferably an amount in the range of 50 to 90 wt.-%, even more preferably an amount in the range of 70 to 85 wt.-%, based on the weight of the electrolyte (EL).

**[0039]** It is appreciated that the at least one medium (M) is selected from the group consisting of water, alcohols, ethers, esters, carboxylic acids, and mixtures thereof, like  $\text{C}_1$  to  $\text{C}_8$  aliphatic alcohols,  $\text{C}_1$  to  $\text{C}_8$  aliphatic ethers,  $\text{C}_1$  to  $\text{C}_8$  aliphatic esters,  $\text{C}_1$  to  $\text{C}_8$  aliphatic carboxylic acids, and mixtures thereof, preferably from the group consisting of water, alcohols, ethers, and mixtures thereof, like  $\text{C}_1$  to  $\text{C}_8$  aliphatic alcohols,  $\text{C}_1$  to  $\text{C}_8$  aliphatic ethers, and mixtures thereof. In a preferred embodiment the at least one medium (M) is water.

**[0040]** In a preferred embodiment the term "water" is directed at deionized water.

**[0041]** In an embodiment the at least one medium (M) is an electrolyte which is compounded with the at least one acid compound (A), the at least one fluoride compound (F), the at least one complexing agent (CA) and optionally additives (AD) to form the electrolyte (EL). In a preferred embodiment the at least one medium (M) is water which is compounded with the at least one acid compound (A), the at least one fluoride compound (F),

the at least one complexing agent (CA) and optionally additives (AD) to form the electrolyte (EL). In other words in a preferred embodiment the electrolyte (EL) is an aqueous electrolyte comprising the at least one acid compound (A), the at least one fluoride compound (F) and the at least one complexing agent (CA).

### The Additives (AD)

**[0042]** The electrolyte (EL) may comprise additional additives (AD) that are applied in the electrolytic polishing of metallic substrates to benefit the process. Typical additives are known to a person skilled in the art of electrolytic polishing of metallic substrates and are applied according to needs. Typical additives for the electrolytic polishing of metallic substrates are for example surfactants, polyvalent alcohols, silicates, thickeners, and the like.

**[0043]** It is appreciated that the additives (AD) are present in the electrolyte (EL) in an amount of not more than 25 wt.-%, preferably in an amount of not more than 15 wt.-%, more preferably in an amount of not more than 10 wt.-%, even more preferably in an amount of not more than 5 wt.-%, yet even more preferably in an amount of not more than 2 wt.-%, like an amount in the range of 0.01 to 25 wt.-%, preferably an amount in the range of 0.01 to 10 wt.-%, more preferably an amount in the range of 0.01 to 5 wt.-%, even more preferably an amount in the range of 0.01 to 2 wt.-%, based on the weight of the electrolyte (EL).

### THE PROCESS FOR THE ELECTROLYTIC POLISHING OF A METALLIC SUBSTRATE

**[0044]** The invention is further directed at a process for the electrolytic polishing of a metallic substrate.

**[0045]** A process for the electrolytic polishing of a metallic substrate is described comprising the steps of

- (i) providing an electrolyte (EL) as described herein in an electrolytic cell comprising at least one electrode,
- (ii) disposing a metallic substrate as an anode in the electrolytic cell,
- (iii) applying a current from a power source between the at least one electrode and the metallic substrate, and
- (iv) immersing the metallic substrate in the electrolyte (EL).

**[0046]** The term "electrolytic cell" as used according to the present invention is directed at an electrochemical cell that undergoes a redox reaction when electrical energy is applied. In particular an electrochemical cell containing an electrolyte through which an externally generated electric current is passed by a system of electrodes in order to produce an electrochemical reaction. The electrolytic cell can be used to decompose a metallic substrate, in a process called electrolysis.

**[0047]** In accordance with the present invention the electrolyte (EL) is provided in an electrolytic cell which also contains a suitable cathode. In a preferred embodiment the electrolytic cell comprises a container receiving the electrolyte wherein the container is made the cathode of the electrolytic cell. However, it is also possible that at least one separate electrode is present in the electrolytic cell which is made the cathode of the electrolytic cell. Furthermore, it is also possible that the electrolytic cell comprises a container receiving the electrolyte and at least one separate electrode, wherein both container and the at least one separate electrode are made the cathode of the electrolytic cell. The cathode material is not critical and suitable materials include copper, nickel, mild steel, stainless steel, graphite, carbon and the like.

**[0048]** In a preferred embodiment the surface of the cathode and the surface of the anode have a surface ratio of at least 10:1, preferably a surface ratio of at least 12:1, even more preferably a surface ratio of at least 15:1, like a surface ratio in the range of 10:1 to 100:1, preferably a surface ratio in the range of 12:1 to 100:1, more preferably a surface ratio in the range of 12:1 to 50:1, even more preferably a surface ratio in the range of 12:1 to 20:1.

**[0049]** In a preferred embodiment the current from a power source is applied between the at least one electrode and the metallic substrate, i.e. between the cathode and the anode of the electrolytic cell before the metallic substrate is immersed in the electrolyte (EL). In other words in a preferred embodiment process step (iii) is conducted before process step (iv). However, it is also possible that the current from a power source is applied between the at least one electrode and the metallic substrate, i.e. between the cathode and the anode of the electrolytic cell after the metallic substrate has been immersed in the electrolyte (EL). In other words in a further embodiment process step (iii) is conducted after process step (iv).

**[0050]** The composition of the electrolyte (EL) is critical. It is to be understood that the information provided above and below with respect to the electrolyte (EL) mutually applies to the inventive process for the electrolytic polishing of a metallic substrate in presence of the electrolyte (EL). Thus, the electrolyte (EL) for the electrolytic polishing of a metallic substrate comprises at least one acid compound (A), at least one fluoride compound (F), and at least one complexing agent (CA).

**[0051]** In a preferred embodiment the electrolyte (EL) for the electrolytic polishing of a metallic substrate consists of at least one acid compound (A), at least one fluoride compound (F), at least one complexing agent (CA), at least one medium (M), and optionally additives (AD).

**[0052]** It is to be understood that the information provided above and below with respect to the at least one acid compound (A), the at least one fluoride compound (F), the at least one complexing agent (CA), the at least one medium (M) and optionally additives (AD) mutually applies to the inventive process for the electrolytic pol-

ishing of a metallic substrate in presence of at least one acid compound (A), at least one fluoride compound (F), at least one complexing agent (CA), at least one medium (M) and/or optionally additives (AD).

**[0053]** It is an advantage of the present invention that the process for the electrolytic polishing of a metallic substrate can inter alia be applied to metallic substrates with complex surfaces. Thus, the metallic substrate may be in any form such as, for example, bars, plates, flat sheets, sheets of expanded metal, cuboids, or complex structures.

**[0054]** The term "metallic substrate" as used herein is meant to encompass substrates comprising at least one conductive metal or metal alloy. Preferably the metallic substrate consists of at least one conductive metal or metal alloy. It is appreciated that the metallic substrate comprises, preferably consists of, metals selected from the group consisting of aluminium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, niobium, molybdenum, silver, hafnium, tungsten, platinum, gold, steel and combinations thereof, such as alloys, preferably selected from the group consisting of aluminium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, niobium, molybdenum, steel and combinations thereof, such as alloys, more preferably selected from the group consisting of aluminium, titanium and vanadium, and combinations thereof, such as alloys. In a preferred embodiment the metal substrate is selected from the group consisting of Ti-6Al-4V, AlSi<sub>10</sub>Mg, AlSi<sub>7</sub>, Inconel 718, AlMgSc, and combinations thereof.

**[0055]** It has been found that the process results in an excellent reduction of surface roughness both at high voltages and at low voltages.

**[0056]** It is appreciated that the current is applied at a voltage of not more than 100 V, preferably of not more than 80 V, more preferably of not more than 50 V, even more preferably of not more than 20 V, like in the range of 1 to 100 V, preferably in the range of 1 to 80 V, more preferably in the range of 1 to 50 V, even more preferably in the range of 1 to 20 V, yet even more preferably in the range of 5 to 20 V.

**[0057]** However, it is also possible that the current is applied at a voltage of at least 20 V, preferably of at least 50 V, more preferably of at least 100 V, even more preferably of at least 200 V, yet even more preferably of at least 250 V, like in the range of 20 to 800 V, preferably a voltage in the range of 50 to 600 V, more preferably a voltage in the range of 100 to 500 V, even more preferably a voltage in the range of 200 to 400 V, yet even more preferably a voltage in the range of 250 to 350 V.

**[0058]** Furthermore, it is appreciated that the current is applied at a current density in the range of 0.05 to 10 A/cm<sup>2</sup>, preferably at a current density in the range of 0.05 to 5 A/cm<sup>2</sup>, more preferably at a current density in the range of 0.1 to 2.5 A/cm<sup>2</sup>, even more preferably at a current density in the range of 0.1 to 2.0 A/cm<sup>2</sup>, yet even more preferably at a current density in the range of 0.1 to 1.5 A/cm<sup>2</sup>.

**[0059]** The temperature does not appear to be a critical parameter. However, an increased temperature seems to improve the efficiency of the process for the electrolytic polishing of a metallic substrate. It is appreciated that the temperature of the electrolyte is at least 10 °C, preferably is at least 40 °C, more preferably is at least 60 °C, even more preferably is at least 70 °C, yet even more preferably is at least 75 °C, like a temperature in the range of 10 to 95 °C, preferably a temperature in the range of 40 to 95 °C, more preferably a temperature in the range of 60 to 95 °C, even more preferably a temperature in the range of 70 to 90 °C, yet even more preferably a temperature in the range of 75 to 85 °C.

**[0060]** The treatment time is generally within the range of 1 to 240 min. However, the treatment of some metallic substrates may require a shorter or longer treatment for the desired reduction in surface roughness, depending on factors such as initial surface roughness and desired surface roughness, surface area, surface geometry and the like. In a preferred embodiment the current is applied for a time in the range of 1 to 240 min, preferably for a time in the range of 1 to 120 min, more preferably for a time in the range of 1 to 60 min, even preferably for a time in the range of 1 to 30 min, yet even more preferably for a time in the range of 2 to 20 min.

**[0061]** In a preferred embodiment the electrolyte is continuously agitated during the process for the electrolytic polishing of a metallic substrate. There are various methods of agitating an electrolyte during electrolytic polishing of a metallic substrate. The agitation may be achieved by immersing a pressurized gas. Suitable gases for immersion are for example, nitrogen, hydrogen, helium, argon, and combinations thereof. During immersion the pressurized gas is bubbled through the electrolyte. The pressurized gas may have a pressure in the range of 0.01 to 1000 kg/cm<sup>2</sup>, preferably a pressure in the range of 1 to 1000 kg/cm<sup>2</sup>.

**[0062]** It may be beneficial for the process for the electrolytic polishing of a metallic substrate if the metallic substrate is subjected to pre- or post-treatment steps, such as treating the metallic substrate with a cleaning composition. In an embodiment the process for the electrolytic polishing of a metallic substrate comprises a post-treatment step of treating the metallic substrate with a cleaning composition, preferably a post-treatment step of treating the metallic substrate with water, preferably deionized water.

**[0063]** The process for the electrolytic polishing of a metallic substrate provides metallic substrate with reduced surface roughness.

**[0064]** It is appreciated that the average surface roughness ( $R_a$ ) of a metallic substrate treated according to the process for the electrolytic polishing of a metallic substrate described is reduced by at least 0.1 µm, preferably is reduced by at least 0.5 µm, even more preferably is reduced by at least 1.0 µm, like in the range of 0.1 to 100 µm, preferably in the range of 0.5 to 10 µm, even more preferably in the range of 1.0 to 5.0 µm.

[0065] Furthermore, it is appreciated that from the process for the electrolytic polishing of a metallic substrate described a metallic substrate is obtained with an average surface roughness ( $R_a$ ) of not more than 10  $\mu\text{m}$ , preferably of not more than 5  $\mu\text{m}$ , more preferably of not more than 1  $\mu\text{m}$ , even more preferably of not more than 0.5  $\mu\text{m}$ , yet even more preferably of not more than 0.1  $\mu\text{m}$ , like an average surface roughness ( $R_a$ ) in the range of 10 to 0.01  $\mu\text{m}$ , preferably an average surface roughness ( $R_a$ ) in the range of 5 to 0.01  $\mu\text{m}$ , more preferably an average surface roughness ( $R_a$ ) in the range of 1 to 0.01  $\mu\text{m}$ , even more preferably an average surface roughness ( $R_a$ ) in the range of 0.5 to 0.01  $\mu\text{m}$ , yet even more preferably an average surface roughness ( $R_a$ ) in the range of 0.1 to 0.01  $\mu\text{m}$ .

[0066] The electrolyte (EL) is described in more detail above and below in particular in the section "THE ELECTROLYTE".

#### USE OF THE COMPLEXING AGENT (CA)

[0067] The electrolyte (EL) can be applied for electrolytic polishing of metallic substrates comprising metals or metal alloys. It is a finding of the present invention that the efficiency of surface roughness reduction in an electrolytic polishing process of a metallic substrate can be improved when providing at least one complexing agent (CA). In addition hereto it is a finding of the present invention that the lifetime of an electrolyte can be increased when providing at least one complexing agent (CA).

[0068] The invention is further directed at the use of at least one complexing agent (CA) in an electrolyte to increase the efficiency of surface roughness reduction in an electrolytic polishing process of a metallic substrate.

[0069] The invention is further directed at the use of at least one complexing agent (CA) in an electrolyte to increase the lifetime of the electrolyte when applied in an electrolytic polishing process of a metallic substrate.

[0070] The at least one complexing agent (CA) is described in more detail above and below, in particular in the section "The Complexing Agent (CA)".

#### FIGURES

[0071]

**Figure 1** depicts a SEM image of the metallic substrate Ti-6Al-4V before being treated in the process according to Example 1. The SEM image provides a 100 fold magnification and has been acquired at a voltage of 15,000 kV and a working distance of 4.5 mm.

**Figure 2** depicts a SEM image of the metallic substrate Ti-6Al-4V after being treated in the process according to Example 1. The SEM image provides a 100 fold magnification and has been acquired at a voltage of 15,000 kV and a working distance of 8.9

mm.

**Figure 3** depicts a SEM image of the metallic substrate Ti-6Al-4V after being treated in the process according to Example 1. The SEM image provides a 10,000 fold magnification and has been acquired at a voltage of 15,000 kV and a working distance of 5.4 mm.

**Figure 4** depicts a SEM image of a metallic substrate Ti-6Al-4V after being treated in the process according to Example 2. The SEM image provides a 100 fold magnification and has been acquired at a voltage of 15,000 kV and a working distance of 10.4 mm.

**Figure 5** depicts a SEM image of a metallic substrate Ti-6Al-4V after being treated in the process according to Example 2. The SEM image provides a 10,000 fold magnification and has been acquired at a voltage of 15,000 kV and a working distance of 10.4 mm.

#### EXAMPLES

##### Definitions and Measuring Methods

[0072] The **average surface roughness ( $R_a$ )** is determined according to DIN EN 4287:1998-10 using the tactile incision technique according to DIN EN ISO 3274 (Hommel Tester T1000 Wave of Jenoptik, tipradius 5  $\mu\text{m}$ , taper angle 90°) **The pH** is determined according to DIN 19261:2005-6.

##### Example 1

[0073] A metallic substrate in form of a 32 mm x 16 mm x 30 mm metal plate of Ti-6Al-4V with an initial average surface roughness of  $R_a = 16.0 \mu\text{m}$  is disposed as an anode in an electrolytic cell comprising a stainless steel cathode. A current of 20 V is applied from a direct current power source between the cathode and the metallic substrate. The metallic substrate is immersed in an electrolyte consisting of 6 wt.-%  $\text{NH}_4\text{F}$ , 4 wt.-%  $\text{H}_2\text{SO}_4$  and 1 wt.-% MGDA. The electrolyte has a pH of 3.5. The metallic substrate is treated for 10 min. A final average surface roughness of  $R_a = 0.9 \mu\text{m}$  is achieved.

##### Example 2

[0074] A metallic substrate in form of a 116 mm x 25 mm x 30 mm metal plate of Ti-6Al-4V with an initial averaged surface roughness of  $R_a = 16.0 \mu\text{m}$  is disposed as an anode in an electrolytic cell comprising a stainless steel cathode. A current of 20 V is applied from a direct current power source between the cathode and the metallic substrate. The metallic substrate is immersed in an electrolyte consisting of 6 wt.-%  $\text{NH}_4\text{F}$  and 1 wt.-%  $\text{H}_2\text{SO}_4$ . The electrolyte has a pH of 3.5. The metallic substrate is treated for 10 min. A final average surface rough-



ness of  $R_a = 9.3 \mu\text{m}$  is achieved. The building of oxide layers can be partially be observed on the surface.

### Example 3

**[0075]** A metallic substrate in form of a 50 mm x 10 mm x 20 mm metal plate of  $\text{AlSi}_{10}\text{Mg}$  with an initial averaged surface roughness of  $R_a = 16.4 \mu\text{m}$  is disposed as an anode in an electrolytic cell comprising a stainless steel cathode. A current of 20 V is applied from a direct current power source between the cathode and the metallic substrate. The metallic substrate is immersed in an electrolyte consisting of 6 wt.-%  $\text{NH}_4\text{F}$ , 4 wt.-%  $\text{H}_2\text{SO}_4$  and 1 wt.-% MGDA. The electrolyte has a pH of 3.5. The metallic substrate is treated for 10 min. A final average surface roughness of  $R_a = 4.5 \mu\text{m}$  is achieved.

### Claims

1. Electrolyte (EL) for the electrolytic polishing of a metallic substrate comprising

- (i) at least one acid compound (A),
- (ii) at least one fluoride compound (F), and
- (iii) at least one complexing agent (CA).

2. Electrolyte (EL) according to claim 1, consisting of

- (i) at least one acid compound (A),
- (ii) at least one fluoride compound (F),
- (iii) at least one complexing agent (CA),
- (iv) at least one medium (M), and
- (v) optionally additives (AD).

3. Electrolyte (EL) according to any one of previous claims 1 or 2, wherein

- (i) the at least one acid compound (A) is comprised in an amount of not more than 20 wt.-%, preferably in an amount of not more than 15 wt.-%, more preferably in an amount of not more than 10 wt.-%, even more preferably in an amount of not more than 5 wt.-%, like an amount in the range of in the range of 0.05 to 20 wt.-%, preferably in the range of 0.5 to 15 wt.-%" more preferably in the range of 1 to 10 wt.-%, even more preferably in the range of 1 to 5 wt.-%, and/or

- (ii) the at least one fluoride compound (F) is comprised in an amount of not more than 40 wt.-%, preferably in an amount of not more than 30 wt.-%, more preferably in an amount of not more than 15 wt.-%, even more preferably in an amount of not more than 10 wt.-%, like an amount in the range of in the range of 1 to 40 wt.-%, preferably in the range of 1 to 30 wt.-%" more preferably in the range of 2 to 15 wt.-%, even more preferably in the range of 4 to 10 wt.-%, and/or

%, even more preferably in the range of 4 to 10 wt.-%, and/or

(iii) the at least one complexing agent (CA) is comprised in an amount of not more than 30 wt.-%, preferably in an amount of not more than 20 wt.-%, more preferably in an amount of not more than 10 wt.-%, even more preferably in an amount of not more than 5 wt.-%, like an amount in the range of in the range of 0.5 to 30 wt.-%, preferably in the range of 0.5 to 20 wt.-%" more preferably in the range of 0.5 to 10 wt.-%, even more preferably in the range of 0.5 to 5 wt.-%, yet even more preferably in the range of 1 to 3 wt.-%, and/or

(iv) the at least one medium (M) in an amount of at least 10 wt.-%, preferably in an amount of at least 30 wt.-%, more preferably in an amount of at least 50 wt.-%, even more preferably in an amount of at least 70 wt.-%, like an amount in the range of 10 to 98.5 wt.-%, preferably in the range of 30 to 95 wt.-%, more preferably in the range of 50 to 90 wt.-%, even more preferably in the range of 70 to 85 wt.-%, and/or

(v) additives (AD) in an amount of not more than 25 wt.-%, preferably in an amount of not more than 15 wt.-%, more preferably in an amount of not more than 10 wt.-%, even more preferably in an amount of not more than 5 wt.-%, yet even more preferably in an amount of not more than 2 wt.-%, like an amount in the range of 0.01 to 25 wt.-%, preferably in the range of 0.01 to 10 wt.-%, more preferably in the range of 0.01 to 5 wt.-%, even more preferably in the range of 0.01 to 2 wt.-%, based on the weight of the electrolyte (EL), based on the weight of the electrolyte (EL).

4. Electrolyte (EL) according to any one of previous claims 1 to 3, wherein the at least one acid compound (A) is selected from the group consisting of inorganic or organic acids such as sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, formic acid, acetic acid propionic acid, or mixtures thereof, preferably is selected from the group consisting of sulfuric acid, nitric acid, phosphoric acid, or mixtures thereof, more preferably is sulfuric acid.

5. Electrolyte according to any one of previous claims 1 to 4, wherein the at least one fluoride compound (F) is selected from the group consisting of ammonium fluoride, sodium fluoride, potassium fluoride, magnesium fluoride, calcium fluoride, trifluoroacetic acid, or mixtures thereof, preferably is selected from the group consisting of ammonium fluoride, sodium fluoride, potassium fluoride, magnesium fluoride,

calcium fluoride, or mixtures thereof, more preferably is ammonium fluoride.

6. Electrolyte according to any one of previous claims 1 to 5, wherein the at least one complexing agent (CA) is selected from the group consisting of methylglycindiacyetic acid (MGDA), ethylenediaminetetraacetate (EDTA), diethylenetriaminepentakis(methylenephosphonic acid (DTPMP) aminopolycarboxylic acids (APC) diethylenetriaminepentaacetate (DTPA), nitrilotriacetate (NTA), triphosphate, 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA), phosphonate, diethylenetriaminepentakis(methylenephosphonic acid (DTPMP), gluconic acid,  $\beta$ -alaninediacetic acid (ADA), N-bis[2-(1,2-dicarboxyethoxy)ethyl]glycine (BCA5), N-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid (BCA6), tetrakis(2-hydroxypropyl)ethylenediamine (THPED), N-(Hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA) or mixtures thereof, preferably is selected from the group consisting of methylglycindiacyetic acid (MGDA), ethylenediaminetetraacetate (EDTA), diethylenetriaminepentakis(methylenephosphonic acid (DTPMP) aminopolycarboxylic acids (APC) diethylenetriaminepentaacetate (DTPA), diethylenetriaminepentakis(methylenephosphonic acid (DTPMP), tetrakis(2-hydroxypropyl)ethylenediamine (THPED), N-(hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA), or mixtures thereof, more preferably is methylglycindiacyetic acid (MGDA).

7. Process for the electrolytic polishing of a metallic substrate comprising the steps of

- (i) providing an electrolyte (EL) according to any of previous claims 1 to 6 in an electrolytic cell comprising at least one electrode,
- (ii) disposing a metallic substrate as an anode in the electrolytic cell,
- (iii) applying a current from a power source between the at least one electrode and the metallic substrate, and
- (iv) immersing the metallic substrate in the electrolyte (EL).

8. Process according to claim 7, wherein the current is applied at a voltage of not more than 100 V, preferably of not more than 80 V, more preferably of not more than 50 V, even more preferably of not more than 20 V, like in the range of 1 to 100 V, preferably in the range of 1 to 80 V, more preferably in the range of 1 to 50 V, even more preferably in the range of 1 to 20 V, yet even more preferably in the range of 5 to 20 V.

9. Process according to any one of previous claims 7 or 8, wherein the electrolyte has a temperature in the range of 10 to 95 °C, preferably in the range of

40 to 95 °C, more preferably in the range of 60 to 95 °C, even more preferably in the range of 70 to 90 °C, yet even more preferably in the range of 75 to 85 °C.

10. Process according to any one of previous claims 7 to 9, wherein the current is applied at a current density in the range of 0.05 to 10 A/cm<sup>2</sup>, preferably at a current density in the range of 0.05 to 5 A/cm<sup>2</sup>, more preferably at a current density in the range of 0.1 to 2.5 A/cm<sup>2</sup>, even more preferably at a current density in the range of 0.1 to 2.0 A/cm<sup>2</sup>, yet even more preferably at a current density in the range of 0.1 to 1.5 A/cm<sup>2</sup>.

11. Process according to any one of previous claims 7 to 9, wherein the current is applied for a time in the range of 1 to 240 min, preferably in the range of 1 to 120 min, more preferably in the range of 1 to 60 min, even preferably in the range of 1 to 30 min, yet even more preferably in the range of 2 to 20 min.

12. Use of at least one complexing agent (CA) in an electrolyte to increase the efficiency of surface roughness reduction in an electrolytic polishing process of a metallic substrate.

13. Use of at least one complexing agent (CA) in an electrolyte to increase the lifetime of the electrolyte when applied in an electrolytic polishing process of a metallic substrate.

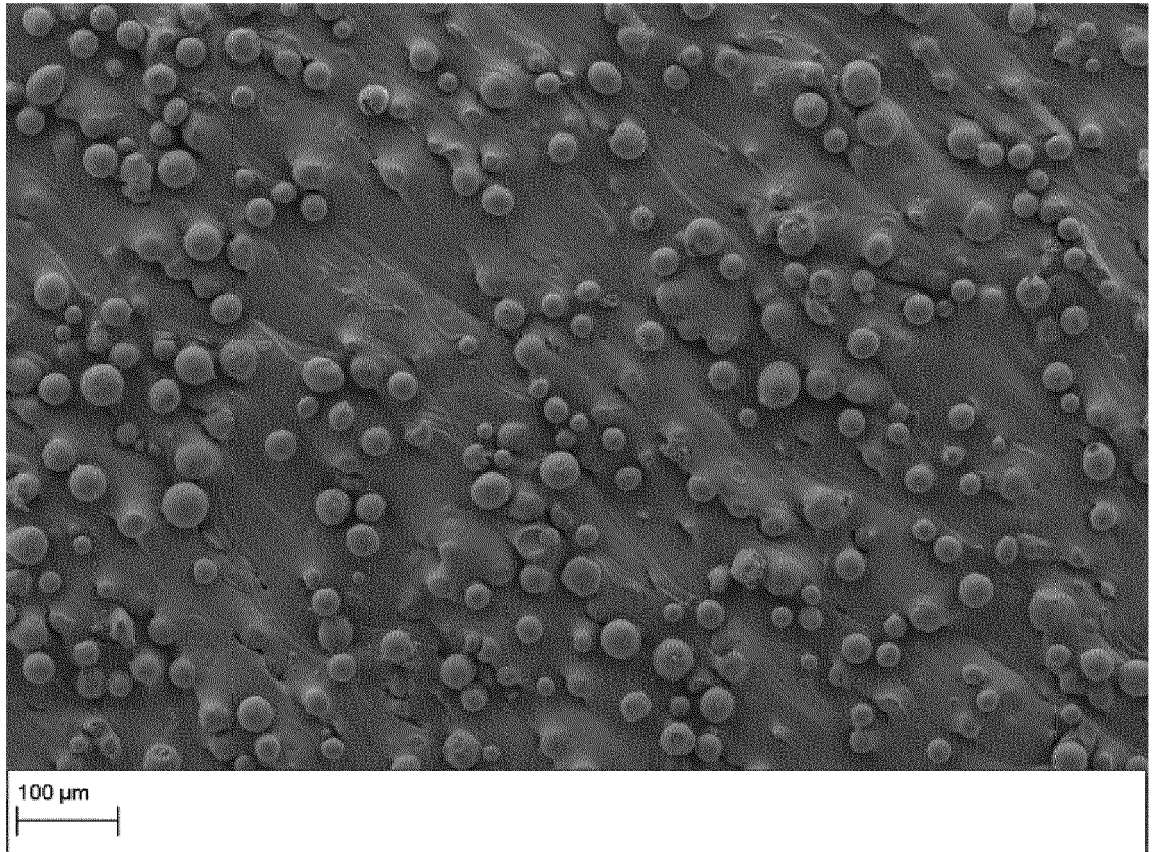


Fig. 1

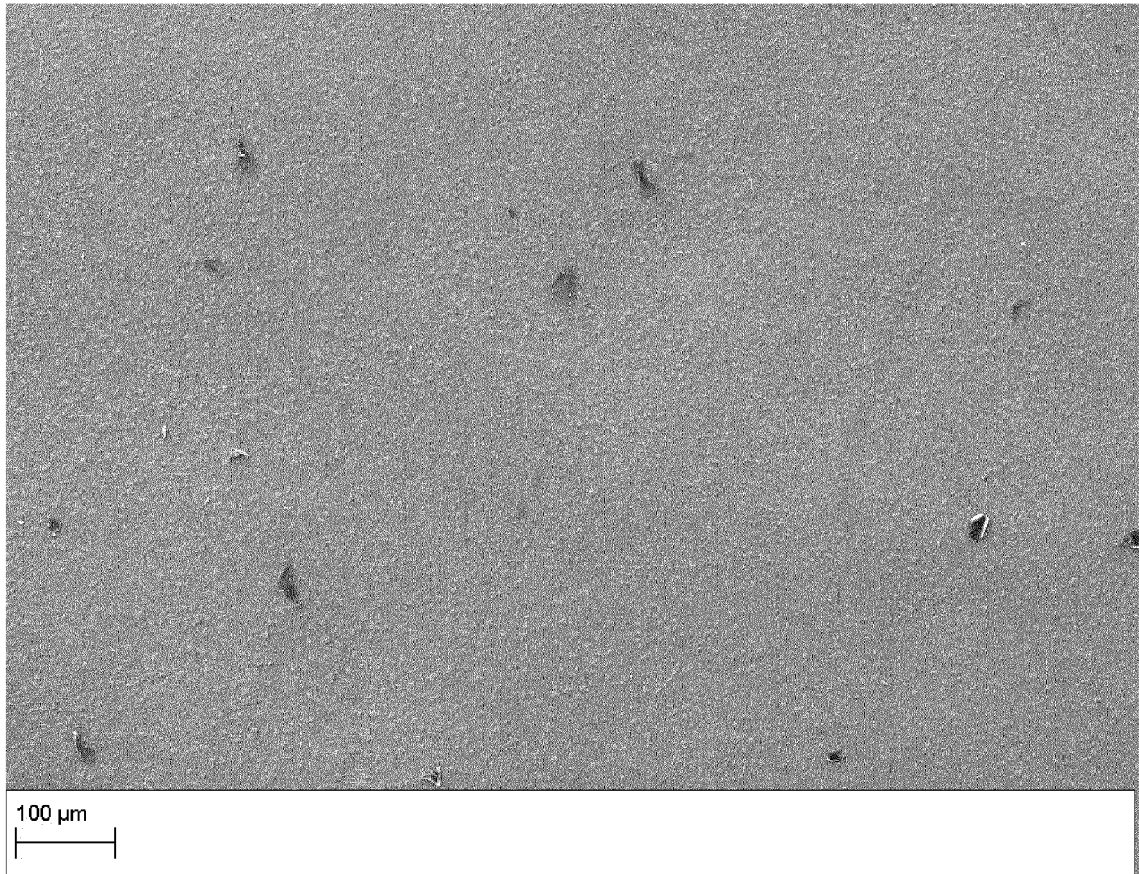


Fig. 2

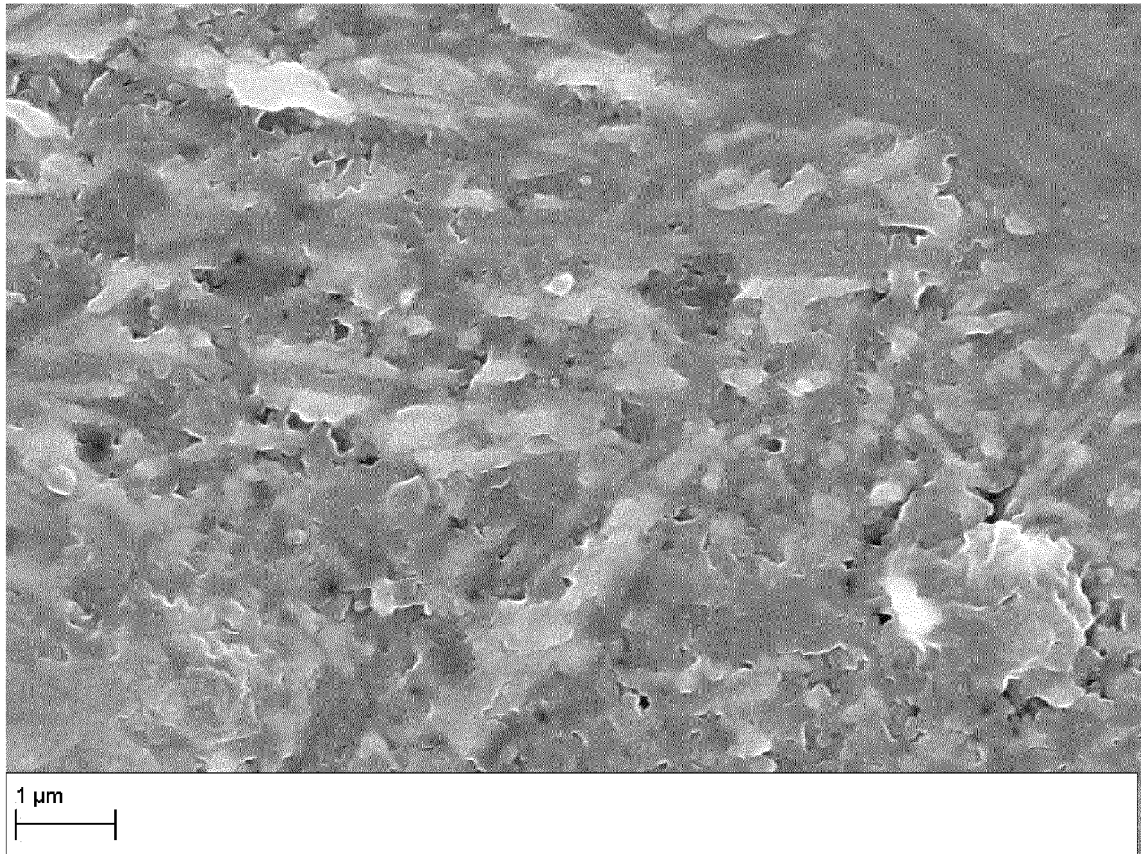


Fig. 3

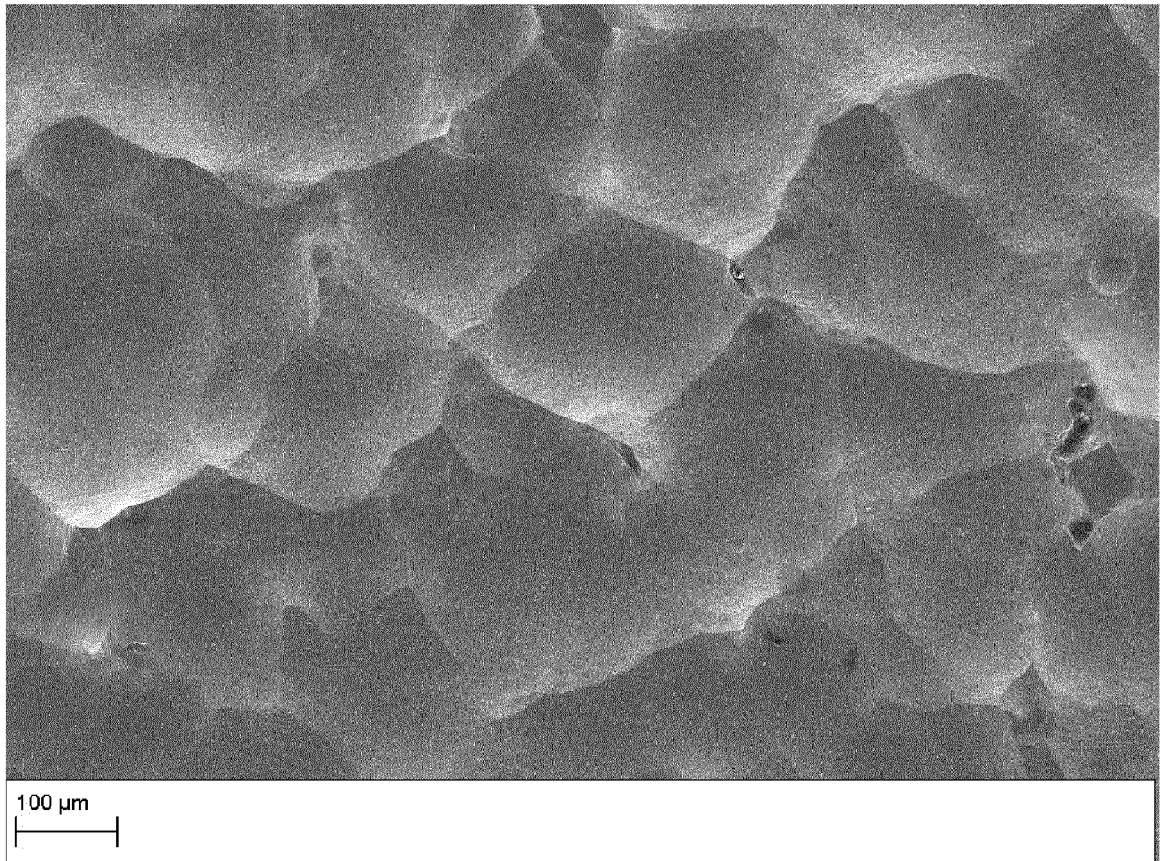


Fig. 4



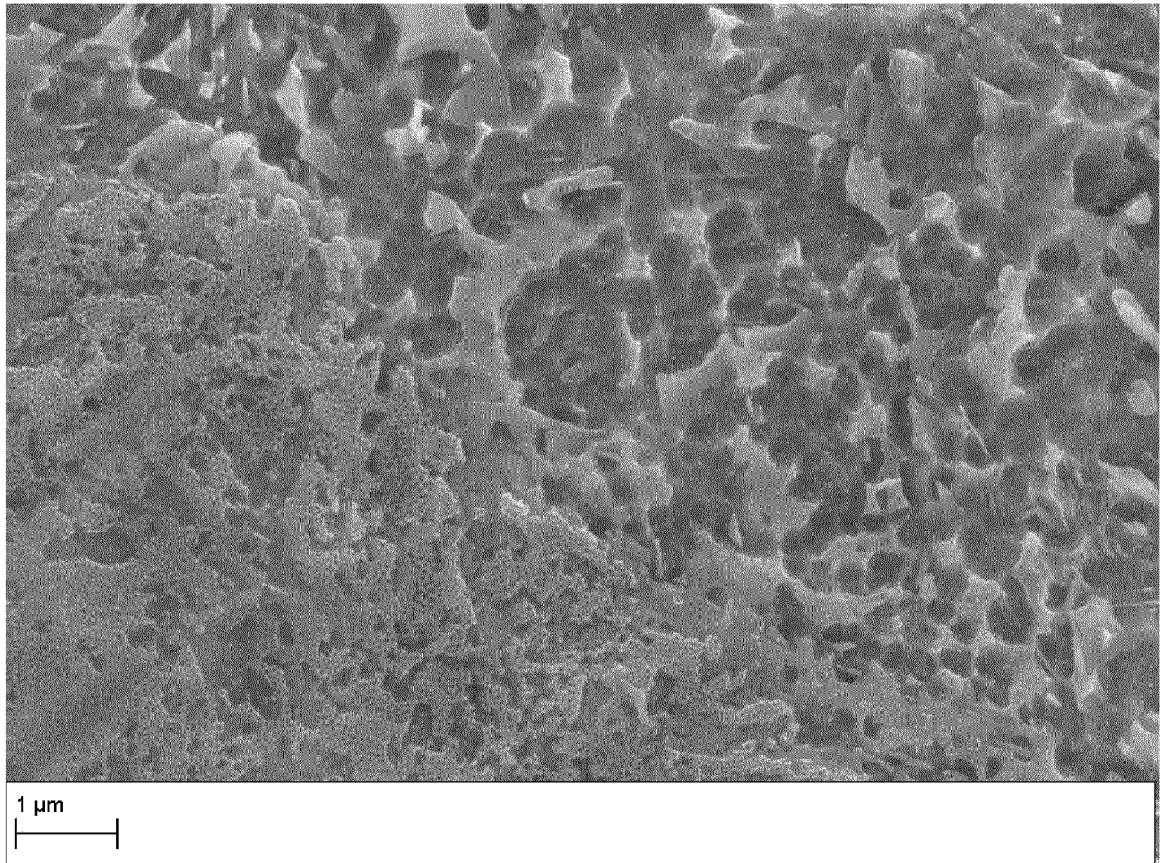


Fig. 5



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