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(54) SURFACE PREPARATION FOR ELECTROLYTIC INORGANIC FINISH COATING

(57) The present disclosure relates to substrate surface treatment methods and compositions. In at least one aspect, a method includes degreasing a metal substrate; performing a first alkaline cleaning on the metal substrate; etching the metal substrate by electropolishing techniques or with an alkaline etchant solution to form an etched metal substrate, wherein the etched metal substrate comprises an average surface roughness (R_a) of about 8 μin (0.2 μm) to about 16 μin (0.4 μm); deoxidizing the etched metal substrate to form a processed metal substrate; performing alkaline cleaning on the processed metal substrate; optionally performing etch-cleaning and deoxidizing if needed to remove oxides and depositing a coating onto the processed metal substrate to form a coated metal substrate.

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Description

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims benefit of and priority to U.S. Provisional Application Serial Number 63/526,368 filed on July 12, 2023, which is hereby incorporated by reference in its entirety.

FIELD

[0002] The present disclosure relates to substrate surface treatment methods and compositions.

BACKGROUND

[0003] Production of aircraft requires an efficient assembly process for constructing large scale metal items or structural components of said items. In production of aircraft, holes in each component may be drilled separately, before the components are brought together in a stack and affixed together, which eliminates conventional requirements of components having to be stacked and aligned twice, as is associated with traditional methods of assembly. However, while efficient assembly processes reduce production time and expense, the large scale metal items and structural components produced from such assembly processes remain susceptible to corrosion and environmental degradation throughout processing, assembly, and use.

[0004] Application of inorganic finishes are commonly used to reduce and/or eliminate corrosion and environmental degradation that can result from processing, assembly, and use of such large scale metal items and structural components. However, the processes and surface treatments commonly implemented to apply such coatings (e.g., acid pickle) can have undesirable effects on the surface of the substrate in which the coating is applied.

[0005] Thus, there is a need to develop new substrate surface treatment methods and compositions for the application of inorganic finishes onto large scale metal items and structural components.

[0006] References for citing in an information disclosure statement (37 C.F.R. 1.97(h)): U.S. Patent Nos. 11,155,928; 11,303,047; 11,661,665; U.S. Application Nos. 16/721,081; 12/137,948.

SUMMARY

[0007] The present disclosure relates to substrate surface treatment methods and compositions.

[0008] In at least one aspect, a method includes degreasing a metal substrate; performing a first alkaline cleaning on the metal substrate; etching the metal substrate with an alkaline etchant solution to form an etched metal substrate, wherein the etched metal substrate comprises an average surface roughness (R_a) of about 250 μin (6.4 μm) or less; deoxidizing the etched metal substrate to form a processed metal substrate; performing a second alkaline cleaning on the processed metal substrate; and optionally performing additional etch cleaning and deoxidizing to remove oxides and depositing a coating onto the processed metal substrate to form a coated metal substrate.

[0009] In at least one aspect, a method includes degreasing a metal substrate; performing a first alkaline cleaning on the metal substrate; etching the metal substrate with an alkaline etchant solution to form an etched metal substrate, the alkaline etchant solution comprising about 2 vol % to about 6 vol % of triethanolamine, about 2 vol % to about 30 vol % of a sodium sulfide additive, about 10 vol % to about 40 vol % of 50% sodium hydroxide, about 75 g/L or less of dissolved metal content, and about 6 g/L or less of ethylenediaminetetraacidic acid (EDTA); deoxidizing the etched metal substrate with a deoxidizing solution comprising about 40 vol % to about 60 vol % of nitric acid, which may be used alone or in combination with iron based or chromated deoxidizing solutions, to form a processed metal substrate; performing a second alkaline cleaning on the processed metal substrate; optionally performing additional etch cleaning with an alkaline etchant solution to form an etched metal substrate, the alkaline etchant solution comprising about 2 vol % to about 6 vol % of triethanolamine, about 2 vol % to about 30 vol % of a sodium sulfide additive, about 10 vol % to about 40 vol % of 50% sodium hydroxide, about 75 g/L or less of dissolved metal content, and about 6 g/L or less of ethylenediaminetetraacidic acid (EDTA); deoxidizing the etched metal substrate with a deoxidizing solution comprising about 40 vol % to about 60 vol % of nitric acid, which may be used alone or in combination with iron based or chromated deoxidizing solutions, to form a processed metal substrate and depositing a coating onto the deoxidized metal substrate to form a coated metal substrate.

[0010] In at least one aspect, a method includes degreasing a metal substrate; performing a first alkaline cleaning on the metal substrate; etching the metal substrate with an alkaline etchant solution to form an etched metal substrate, the alkaline etchant solution comprising about 2 vol % to about 6 vol % of triethanolamine, about 2 vol % to about 30 vol % of a sodium sulfide additive, about 10 vol % to about 40 vol % of 50% sodium hydroxide, about 75 g/L or less of dissolved metal content, and about 6 g/L or less of ethylenediaminetetraacidic acid (EDTA); deoxidizing the etched metal substrate with a deoxidizing solution to form a processed metal substrate, the deoxidizing solution comprising about 40 vol % to about 60 vol % of nitric acid; performing a second alkaline cleaning on the processed metal substrate; optionally performing alkaline etch cleaning with said alkaline etchant and deoxidizing the etched metal substrate, the deoxidizing solution comprising about 40 vol% to 60 vol% of nitric acid, used alone or in combination with iron based for chromated deoxidizers to remove oxides if needed and depositing a coating onto the processed metal substrate to form a coated metal substrate, wherein depositing a coating onto the processed metal substrate comprises electrolytically depositing an inorganic finish thereon, the electrolytic deposition of the inorganic finish comprising attaching the processed metal substrate to two or more counter electrodes, electrically connecting the processed metal substrate to a power supply, immersing the processed metal substrate within a inorganic finishing solution, applying a current density to the processed metal substrate to form a coated metal substrate, and rinsing the coated metal substrate.

[0011] In at least one aspect, a coated metal substrate, comprises an etched metal substrate, the etched metal substrate comprising a metal substrate having an average surface roughness of about 79μin (2 μm) to about 8 μin (0.2 μm), wherein the average surface roughness of the metal substrate is the result of etching the metal substrate in an etching solution and deoxidizing the metal substrate in a deoxidation solution comprising about 40 vol % to about 60 vol % of nitric acid; and a inorganic finish disposed over the etched metal substrate, wherein the inorganic finish comprises a morphology substantially as shown in Figure 2.

BRIEF DESCRIPTION OF FIGURES

[0012] So that the manner in which the above recited features of the present disclosure can be understood in detail, a more particular description of the disclosure, briefly summarized above, may be had by reference to aspects, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical aspects of this present disclosure and are therefore not to be considered limiting of its scope, for the present disclosure may admit to other equally effective aspects.

FIG. 1 is a cross-sectional schematic view of the structural assembly of FIG. 1 prior to fastening with the fastening system.

FIG. 2 shows a representative example of an aluminum substrate which has undergone chemical etching with an alkaline etchant composition and deoxidation using a deoxidation solution having 50 vol % HNO_3.

FIG. 3 shows a representative example of an aluminum substrate which has undergone chemical etching with an acid pickle composition and deoxidation using a deoxidation solution having a chromated deoxidizing component.

FIG. 4 shows a 7075-T6 aluminum metal substrate, which has undergone chemical etching with an alkaline etchant composition, deoxidation using a deoxidation solution having 50 vol % HNO_3, and electrolytically coated with an inorganic finish, after 336 hours within a neutral salt fog environment.

FIG. 5 shows a 2024-T3 aluminum metal substrate, which has undergone chemical etching with an alkaline etchant composition, deoxidation using a deoxidation solution having 50 vol % HNO_3, and electrolytically coated with an inorganic finish, after 336 hours within a neutral salt fog environment.

DETAILED DESCRIPTION

[0013] includes pre-forming (e.g., pre-drilling) the holes of the different structural elements (also referred to herein as substrate(s)) separately (*e.g.,* at remote geographic locations, different times, different locations within the same geographic region, etc.), and then once the holes are formed, bringing the structural elements together and assembling (*e.g.*, aligning, stacking, and fastening) them to form a structural assembly..

[0014] As schematically illustrated in FIG. 1, an apparatus comprises structural assembly 12 and a fastening system. The structural assembly 12 comprises at least two structural elements (e.g., first structural element 16 and second structural element 18) and the at least two structural elements are fastened to one another via the fastening system. In one or more aspects, the structural assembly 12 can be joined together to form one or more components of an aircraft, a spacecraft, a land vehicle, an engine, a propulsion structure, a space re-entry vehicle and/or structure thereof, a power-generation turbine, or combinations thereof. In some aspects, the structural assembly 12 may be a fitting and/or joint, such as one or more of: a fuel tank joint, wing joint, fuselage joint, side-of-body j oint, and major fitting.

[0015] In the example of FIG. 1, the at least two structural elements comprise two structural elements, the first structural element 16 and second structural element 18. However, in other examples, the structural assembly **12** comprises more than two structural elements, such as three, four, five, six, seven, or eight or more structural components that are fastened together by a fastening system. Additionally, the first structural element **16** further includes a first structural element sidewall **22** and a first structural element hole sidewall **35.** The second structural element **18** further includes a second structural element sidewall **41** and a second structural element hole sidewall **37.** In some such examples, more than two components are pre-formed, stacked, and assembled, and then fastened to one another.

[0016] At least a portion of the second structural element **18** is positioned adjacent to the first structural element **16** such that at least portions of the first structural element **16** and the second structural element **18** directly physically touch/contact one another. Due to their proximity, the first structural element **16** and second structural element **18,** in some examples, comprise components of the same aircraft part (e.g., both of the structural elements may be components of a fuel tank). However, in other examples, the first structural element **16** and second structural element **18** comprise components of different but adjacent aircraft parts (e.g., wing and fuel tank, wing and engine, wing and fuselage, etc.), and in some such examples, the first structural element **16** and second structural element **18** are fastened to one another to couple the different aircraft parts. Together, the first structural element **16** and second structural element **18** form the structural assembly **12.**

[0017] Insome aircraft assembly processes, holes are pre-formed (e.g., pre-drilled, premolded, pre-reamed, or otherwise pre- formed) in the first structural element **16** and second structural element **18** prior to assembling the structural elements into the structural assembly **12.** In particular, a first structural element hole **48** is drilled, molded, reamed, or otherwise formed into the first structural element **16** and a second structural element hole **50** is drilled, molded, reamed, or otherwise formed into the second structural element **18.** Although only one of each of the first structural element hole **48** and second structural element hole **50** are shown in FIG. **1,** in other examples, the first structural element **16** and second structural element **18** include a plurality of the first structural element hole **48** and second structural element hole **50.** In some such examples, the number of first structural element holes **48** and second structural element holes **50** included in the first structural element **16** and second structural element **18** depend on the size and shape of the structural assembly **12** and the desired level of fastening for a particular application.

[0018] Prior to assembly, it may be desirable to deposit a coating onto one or more structural elements of the structural assembly. It will be appreciated to one of ordinary skill in the art that a method of coating a substrate can include a wide variety of method processes depending on the substrate to be coated, the composition of the coating, and the implemented method of coating deposition. In some aspects, the method of depositing a coating onto the one or more structural elements includes one or more substrate cleaning processes, one or more substrate surface preparation processes, and one or more coating deposition processes. Shape and structure of the substrate may be arbitrarily selected in accordance to parameters associated withassembly processes, and is not limited to a planar surface. For example, the substrate may have a non-planar shape, and having a surface onto which the coating may be applied. In one or more aspects, the substrate is a metal substrate selected from aluminum, aluminum alloy, or a mixture thereof.

[0019] In one or more aspects, the metal substrate is subjected to a cleaning step that includes degreasing the substrate. The metal substrate may be degreased using any degreasing agent such as, for example, acetone or an aqueous alkaline degreasing agent. This step may comprise the immersion of the metal substrate in a degreasing agent for about 5 min to about 30 min, manual cleaning with a cloth, and the application of ultrasonic agitation for about 5 min to about 20 min, or until neither oil nor grease remains on their surface. Additionally, after the degreasing step, the metal substrate may be dried, using hot air. In some embodiments, the metal substrate may be cleaned using solvent vapor degreasing, vacuum cycle nucleation (VCN), and combinations thereof.

[0020] In one or more aspects, the metal substrate is subjected to an alkaline cleaning step to form a cleaned metal substrate. The alkaline cleaning may be done by immersing the metal substrate in an aqueous alkaline cleaning agent such as, for example, 38 to 60 g / L of Bonderite C-AK 4215 NC LT Aero and a range of 0 to 0.25% by volume of Bonderite C-AD 4215 Aero during a period ranging from about 5 min to about 30 min. In at least one aspect, the alkaline cleaning is conducted at a temperature of about 40 °C to about 60 °C.

[0021] The cleaned metal substrate may be etched via one or more etching methods known to one of ordinary skill in the art, such as chemical etching, pickling, physical abrasion, mechanical polishing, machining, electropolishing, or combinations thereof.

[0022] In some aspects, the cleaned metal substrate is chemically etched to form an etched metal substrate using an alkaline etchant solution. In at least one aspect, the alkaline etchant solution comprises about 2 vol % to about 6 vol % of triethanolamine, such as about 2 vol % to about 4 vol %. In at least one aspect, the alkaline etchant solution comprises about 2 vol % to about 30 vol % of sodium sulfide additive, such as about 10 vol % to about 20 vol %. In at least one aspect, the alkaline etchant solution comprises about 10 vol % to about 40 vol % of 50 % sodium hydroxide additive, such as about 15 vol % to about 20 vol %. In at least one aspect, the alkaline etchant solution comprises about 0 g/L to about 75 g/L of dissolved metal content, such as about 75 g/L. or less In at least one aspect, the alkaline etchant solution comprises about 6 g/L or less of ethylenediaminetetraacidic acid (EDTA).

[0023] In one or more aspects, the chemical etching of the cleaned metal substrate is conducted via immersing the cleaned metal substrate within the alkaline etchant solution for about 1 min to about 10 min, such as about 2 min to about 7 min. In some aspects, the chemical etching of the cleaned metal substrate includes heating the cleaned metal substrate, the alkaline etchant solution, or both to a temperature of about 30 °C to about 55 °C, such as about 35 °C to about 50 °C.

[0024] In some aspects, the cleaned metal substrate is physically abraded, and/or mechanically polished, to form an etched metal substrate. In one or more aspects, the physical abrasion process can include dry-blasting the metal substrate with one or more of alumina grit, silicon carbide grit, glass beads, steel grit, and combinations thereof. In one or more alternative aspects, the metal substrate may be mechanically and/or manually polished with emery paper and removing the powder remaining on the surface of the metal substrate via any suitable method.

[0025] In some aspects, the cleaned metal substrate is etched via immersion into a nitric acid/HF solution per PS12050.1 Sec. 3.3.1, incorporated herein by reference.

[0026] In one or more aspects, the cleaned metal substrate surface is etched to a desirable surface roughness via any one or more electropolishing methods known to one of ordinary skill in the art.

[0027] In one or more aspects, the etched metal substrate is subjected to a deoxidizing process to form a processed metal substrate. The deoxidizing process may be carried out by immersing the aluminum substrate in a deoxidizing bath containing nitric acid (HNO_3), for example, in a range of 35% to 50% by volume during a period of 1 to 5 minutes and/or a deoxidizing agent such as, for example, a range from 18% to 20% by volume of Bonderite C-IC SmutGo NC Aero, a non-chromium deoxidizer, during a period ranging from 1 to 10 min. In some aspects, the etched metal substrates were deoxidized via immersion into a deoxidizing bath including BONDERITE C-IC SmutGo AERO ACID, a non-chromium deoxidizer for about 4 min to about 12 min. The deoxidizing process may be carried out, for example, at a temperature in the range from about 20 °C to about 50 °C. After that, the aluminum substrate may be rinsed, for example, first with tap water followed by deionized water. In some aspects, deoxidizing the etched metal substrate includes immersing the etched metal substrate within a deoxidizing solution consisting of about 40 vol % to about 60 vol % of nitric acid, such as about 50 vol %. The etched metal substrate is immersed within the deoxidizing solution for about 1 min to about 10 min, such as about 7 min.

[0028] In some aspects, the processed metal substrate is subjected to an alkaline cleaning. The alkaline cleaning may be done by immersing the processed metal substrate in an aqueous alkaline cleaning agent such as, for example, a range from 38 to 60 g / L of Bonderite C-AK 4215 NC LT Aero and a range of 0 to 0.25% by volume of Bonderite C-AD 4215 Aero during a period ranging from about 5 min to about 30 min, such as about 10 min to 20 min. In at least one aspect, the alkaline cleaning is conducted at a temperature of about 35 °C to about 65 °C, such as about 40 °C to about 60 °C, such as about 45 °C to about 55 °C, such as about 47 °C to about 52 °C, wherein the metal substrate, the aqueous alkaline cleaning agent, or both are heated. In some aspects, the alkaline cleaning solution has a pH of about 10 to about 12.

[0029] In some aspects, the surface roughness component of processed metal substrate texture, as defined per ASME B46.1, has an average surface roughness (R_a) of about 500 μin (13 μm) or less, such as about 400 μin(10 μm) or less, such as about 300 μin (7.6 μm) or less, such as about 250 μin (6.4 μm) or less, such as about 200 μin (5.1 μm) or less, such as about 150 μin (3.8 μm) or less, such as about 100 μin (2.5 μm) or less, such as about 50 μin (1.3 μm) or less, such as about 25 μin (0.6 μm) or less, such as about 10 μin (0.3 μm) or less, such as about 5 μin (0.13 μm) or less, such as about 2.5 μin (0.1 μm) or less, such as about 1 μin (0.03 μm) or less. In one or more alternative embodiments, the processed metal substrate has an R_a of about 250 μin (6.4 μm) to about 0.001 μin (0.025 nm) such as about 200 μin (5.1 μm) to about 0.005 μin (0.13 nm), such as about 100 in (2.5 μm) to about 0.01 μin (0.25 nm), such as about 50 μin (1.3 μm) to about 0.025 μin (0.64 nm), such as about 25 μin (0.6 μm) to about 0.05 μin (1.3 nm), such as about 10 μin (0.3 μm) to about 0.075 μin (1.9 nm), such as about 5 μin (0.13 μm) to about 0.1 μin (2.5 nm), such as about 2.5 μin (0.1 μm) to about 0.15 μin (3.8 nm), such as about 2 μin (0.05 μm) to about 0.2 μin (0.01 μm). Optionally, R_a is defined per ASME B46.1-2019.

[0030] In some aspects, the processed metal substrate has a sum of the highest peak and lowest valley (R_t) as determined by R_t=R_v+R_p, wherein R_v is the absolute value of the maximum valley depth measured from R_a and R_p is the maximum peak height measured from R_a. In some aspects, the processed metal substrate has an R_t of about 550 μin (14 μm) to about 710 μin (18 μm), such as about 590 μin (15 μm) to about 670 μin (17 μm). In one or more alternative aspects, the processed metal substrate has an R_t of about 197 μin (5 μm) to about 394 μin (10 μm), alternatively about 158 μin (4 μm) to about 236 μin (6 μm), alternatively about 236 μin (6 μm) to about 315 μin (8 μm).

[0031] In some aspects, a coating is deposited onto the processed metal substrate. The processed metal substrates are affixed to a rack made of a suitable conductive material and immersed in a coating solution. In at least one aspect, the coating solution is an inorganic finish solution. Additionally, a bus bar made from suitable, conductive material is suspended over the inorganic finish solution. Two or more counter electrodes are attached to the bus bar, such that the electrodes are immersed in the solution, no more than 1 foot from the work surfaces. The counter electrodes are immersed at a depth that is shallower than the parts to avoid high current density areas on the parts. Further, the bus bar is electrically connected to the rectifier to impart the desired polarity to the counter electrodes, either cathodic or anodic.

[0032] Additionally, the rack, which the processed metal substrate is affixed, is electrically connected to the rectifier such that the rack is the opposite polarity of the counter electrodes. The rectifier is then powered for the full duration of the inorganic finishing process. At the conclusion of the inorganic finish deposition, the rectifier is powered down, and the rack is disconnected from the rectifier and removed from the inorganic finishing solution. The coated metal substrate is then removed from the rack, rinsed with water and/or any appropriate solvent, and dried via any suitable method know to one of ordinary skill in the art. Alternatively, the rack and bus bar may be electrically connected to the rectifier, and the rectifier powered prior to the immersion of the rack in the inorganic finishing solution. In some embodiments, the rack may be removed at the conclusion of the inorganic finishing process while the rectifier is still on.

[0033] In some aspects, the processed metal substrates are immersed in the inorganic finishing solution and supplied a current density to deposit the coating onto the processed metal substrates. In one or more aspects, the processed metal substrates are immersed in MIL-DTL-81706 Type II conversion coating solution, wherein the conversion coating solution is the inorganic finish solution. In some aspects, the current density supplied to the processed metal substrate during coating deposition is provided by a suitable DC power in a constant current mode, a pulsed current mode, or a combination thereof to provide a cathodic or anodic current density.

[0034] In one or more aspects, the current density supplied to the processed metal substrate is a constant current having a current density of about 0.2 mA/cm^2 to about 0.5 mA/cm^2, such as about 0.25 mA/cm^2 to about 0.45 mA/cm^2. In at least one aspect, the constant current is applied to the processed metal substrate for a duration of about 2 min to about 5 min, such as about 2.5 min to about 4 min.

[0035] In one or more embodiments, a current density is supplied by employing a constant voltage to the processed metal substrate until a desired potential threshold is reached to adequately deposit the coating onto the substrate. In one or more embodiments, the voltage applied to the metal substrate is about 0.5 V to about 10 V, such as about 1.0 V to about 8 V, such as about 1.5 V to about 6 V, such as about V to about 2 V, such as about 4 V to about 3 V. In at least one aspect, the voltage is applied to the processed metal substrate for about 30 seconds to about 10 min, such as about 1 min about 8 min, such as about 2 min to about 6 min, such as about 2 min to about 4 min, such as about 2 min to about 3 min.

[0036] Upon completion of the coating deposition process, the coated metal substrates are removed, rinsed, and dried via any one or more suitable methods known by a person of ordinary skill in the art.

[0037] In some aspects, the coating of the coated metal substrate has a film mass of about 0.05 mg/cm^2 to about 0.11 mg/cm^2, such as about 0.07 mg/cm^2 to about 0.09 mg/cm^2.

[0038] The coating deposited onto the coated metal substrate provides corrosion protection. Operating in accordance to ASTM B117, the coating applied to the processed metal substrate provides corrosion protection in a salt fog environment for a minimum of 336 hours without the formation of pits having a diameter greater than 0.031 in, the formation of more than 5 pits in a 30 in^2 area, and/or the formation of more than 15 pits in a 150 in^2 area. In one or more aspects, the coating deposited onto the coated metal substrate provides such corrosion protection for a minimum of about 336 hours, such as about 500 hours to about 800 hours. Optionally, said corrosion protection is defined in accordance with ASTM B117-19.

Additional Aspects

[0039] The present disclosure provides, among others, the following aspects, each of which may be considered as optionally including any alternate aspects.

Clause 1. A method comprising:

degreasing a metal substrate;
performing a first alkaline cleaning on the metal substrate;
etching the metal substrate with an alkaline etchant solution to form an etched metal substrate, wherein the etched metal substrate comprises an average surface roughness (R_a) of about 250 μin (6.4 μm) or less;
deoxidizing the etched metal substrate to form a processed metal substrate;
optionally performing a second alkaline cleaning on the processed metal substrate; and
depositing a coating onto the processed metal substrate to form a coated metal substrate.

Clause 2. The method of Clause 1, wherein the alkaline etchant solution comprises about 2 vol % to about 6 vol % of triethanolamine, about 2 vol % to about 30 vol % of a sodium sulfide additive, about 10 vol % to about 40 vol % of 50% sodium hydroxide, about 75 g/L or less of dissolved metal content, and about 6 g/L or less of ethylenediaminetetraacidic acid (EDTA)

Clause 3. The method of Clauses 1 or 2, wherein the processed metal substrate comprises an average surface roughness R_a of about 8 μin (0.2 μm) to about 79 μin (2 μm), optionally about 8 μin (0.2 μm) to about 16 μin (0.4 μm).

Clause 4. The method of any of Clauses 1 to 3, wherein the sum of the highest peak and lowest valley (R_t) of the surface of the processed metal substrate is about 158 μin (4 μm) to about 236 μin (6 μm).

Clause 5. The method of any of Clauses 1 to 4, wherein deoxidizing the etched metal substrate comprises immersing the etched metal substrate within a deoxidizing solution comprising about 40 vol % to about 60 vol % of nitric acid.

Clause 6. The method of any of Clauses 1 to 5, wherein depositing a coating onto the processed metal substrate comprises electrolytically depositing an inorganic finish thereon, the electrolytic deposition of the inorganic finish comprising:

attaching the processed metal substrate to a counter electrode,
electrically connecting the processed metal substrate to a power supply,
immersing the processed metal substrate within an inorganic finishing solution,
applying a current density to the processed metal substrate to form a coated metal substrate,

removing the coated metal substrate from the inorganic finishing solution, and
rinsing the coated metal substrate.

Clause 7. The method of any of Clauses 1 to 6, wherein the current density is applied to the processed metal substrate for about 2 min to about 5 min.

Clause 8. The method of any of Clauses 1 to 7, wherein the coating applied to the metal substrate provides corrosion protection in a salt fog environment of 336-hours minimum without pits having a diameter of about 0.031 in or less; fewer than 5-pits in 30-in^2 and fewer than 15-pits in an area of 150-in^2.

Clause 9. The method of any of Clauses 1 to 8, wherein the coating applied to the metal substrate provides corrosion protection in a salt fog environment of 336-hours minimum without pits having a diameter of about 0.031 in or less; fewer than 5-pits in 30-in^2 and fewer than 15-pits in an area of 150-in^2.

Clause 10. A method, comprising:

degreasing a metal substrate;
performing a first alkaline cleaning on the metal substrate;
etching the metal substrate with an alkaline etchant solution to form an etched metal substrate, the alkaline etchant solution comprising about 2 vol % to about 6 vol % of triethanolamine, about 2 vol % to about 30 vol % of a sodium sulfide additive, about 10 vol % to about 40 vol % of 50% sodium hydroxide, about 75 g/L or less of dissolved metal content, and about 6 g/L or less of ethylenediaminetetraacidic acid (EDTA);
deoxidizing the etched metal substrate with a deoxidizing solution comprising about 40 vol % to about 60 vol % of nitric acid, which may be used alone or in combination with iron based or chromated deoxidizing solutions, to form a processed metal substrate;
performing a second alkaline cleaning on the processed metal substrate; optionally performing alkaline etch cleaning with said alkaline etchant;
deoxidizing the etched metal substrate with a deoxidizing solution comprising about 40 vol % to about 60 vol % of nitric acid, which may be used alone or in combination with iron based or chromated deoxidizing solutions to remove oxides if needed, to form a processed metal substrate, and
depositing a coating onto the deoxidized metal substrate to form a coated metal substrate.

Clause 11. The method of Clause 10, wherein depositing a coating onto the processed metal substrate comprises electrolytically depositing an inorganic finish thereon, the electrolytic deposition of the inorganic finish comprising:

attaching the processed metal substrate to a counter electrode, (cathode),
electrically connecting the processed metal substrate to a power supply,
immersing the processed metal substrate within an inorganic finish solution,
applying a current density to the processed metal substrate to form a coated metal substrate,
removing the coated metal substrate from the inorganic finishing solution, and
rinsing the coated metal substrate.

Clause 12. The method of Clauses 10 or 11, wherein the processed metal substrate comprises an R_a of about 8 μin (0.2 μm) to about 79 μin (2 μm), optionally about 8 μin (0.2 μm) to about 16 μin (0.4 μm).

Clause 13. The method of any of Clauses 10 to 12, wherein the Rt of the surface of the processed metal substrate is about 158 μin (4 μm) to about 236 μin (6 μm).

Clause 14. The method of any of Clauses 10 to 13, wherein the current density is applied to the processed metal substrate for about 2 minutes to about 5 minutes.

Clause 15. The method of any of Clauses 10 to 14, wherein the coating applied to the metal substrate provides corrosion protection in a salt fog environment of 336-hours minimum without pits having a diameter of about 0.031 in or less, fewer than 5-pits in 30-in^2, and fewer than 15-pits in an area of 150-in^2.

Clause 16. A method comprising:

degreasing a metal substrate;
performing a first alkaline cleaning on the metal substrate;
etching the metal substrate with an alkaline etchant solution to form an etched metal substrate, the alkaline etchant solution comprising about 2 vol % to about 6 vol % of triethanolamine, about 2 vol % to about 30 vol % of a sodium sulfide additive, about 10 vol % to about 40 vol % (e.g., of 50% sodium hydroxide), about 75 g/L or less of dissolved metal content, and about 6 g/L or less of ethylenediaminetetraacidic acid (EDTA);
deoxidizing the etched metal substrate with a deoxidizing solution to form a processed metal substrate, the deoxidizing solution comprising about 40 vol % to about 60 vol % of nitric acid;

performing a second alkaline cleaning on the processed metal substrate; optionally performing alkaline etch cleaning with said alkaline etchant and deoxidizing the etched metal substrate with a deoxidizing solution comprising about 40 vol % to about 60 vol % of nitric acid, which may be used alone or in combination with iron based or chromated deoxidizing solutions to remove oxides if needed;

depositing a coating onto the processed metal substrate to form a coated metal substrate, wherein depositing a coating onto the processed metal substrate comprises electrolytically depositing an inorganic finish thereon, the electrolytic deposition of the inorganic finish comprising:

attaching the processed metal substrate to two or more counter electrodes,

electrically connecting the processed metal substrate to a power supply,

immersing the processed metal substrate within an inorganic finishing solution,

applying a current density to the processed metal substrate to form a coated metal substrate, and rinsing the coated metal substrate.

Clause 17. The method of Clause 16, wherein the current density applied to the processed metal substrate is about 0.2 mA/cm^2 to about 0.5 mA/cm^2.

Clause 18. The method of Clauses 16 or 17, wherein the current density is applied to the processed metal substrate for about 2 minutes to about 5 minutes.

Clause 19. The method of any of Clauses 16 to 18, wherein the current density is applied to the processed metal substrate as a constant current.

Clause 20. A method comprising:

degreasing a metal substrate;

performing a first alkaline cleaning on the metal substrate;

etching the metal substrate to assure a 5 μm to 13 μm material removal by electropolishing technique or with an alkaline etchant solution to form an etched metal substrate, wherein the etched metal substrate comprises an average surface roughness (R_a) of about 2 μin (0.05 μm) to about 20 μin (0.5 μm);

deoxidizing the etched metal substrate to form a processed metal substrate;

optionally performing a second alkaline cleaning on the processed metal substrate; and

depositing a coating onto the processed metal substrate to form a coated metal substrate.

Clause 21. A coated metal substrate, comprising:

an etched metal substrate, the etched metal substrate comprising a metal substrate having an average surface roughness of about 79 μin (2 μm) to about 8 μin (0.2 μm), wherein:

the average surface roughness of the metal substrate is the result of etching the metal substrate in an etching solution and deoxidizing the metal substrate in a deoxidation solution comprising about 40 vol % to about 60 vol % of nitric acid, and

an inorganic finish disposed over the etched metal substrate, wherein the conversion coating comprises a morphology substantially as shown in Figure 2.

Examples

Sample preparation

[0040] 7050-T7451, 7075-T6, and 2024-T3 aluminum specimens were machined to a desirable size and shape, degreased and cleaned with acetone, and subjected to an alkaline cleaning to produce cleaned aluminum substrates. The cleaned aluminum substrates were chemically etched with alkaline etchant composition including triethanolamine, a sodium sulfide additive, sodium hydroxide, a metal content, and ethylenediaminetetraacidic acid. The etched aluminum substrates were then subjected to a deoxidation process, wherein each sample was immersed within a deoxidation composition having about 50 vol % HNO_3. It is important to note that using a deoxidation composition having about 50 vol % HNO_3 will not etch the aluminum substrate, but will attack intermetallics.

[0041] For the purposes of comparison, additional cleaned aluminum substrates were chemically etched with an acid pickle composition and process, in accordance with PS12050.1. Each of the etched metal specimens were then subjected to a deoxidation process wherein the deoxidation solution a chromated deoxidizing component.

Surface Analysis

[0042] The deoxidized aluminum substrates were observed using a stylus type (surface contact) profilometer and white light interferometery to analyze the surface features of the substrate before and after substrate etching and deoxidizing. The former method for surface roughness characterization involves a stylus of defined diameter in contact with the substrate surface and pulled for a distance of 0.25 mm to 0.8 mm and performed with an instrument such as the Mitutoyo Surftest, whereas the latter method is non-contract surface topography dependent upon interference of light waves from a source and light reflected from the substrate for inference of surface roughness and performed with an instrument such as the Bruker Contour GT-K 3D Optical Microscope. FIG. 2 shows a representative example of an aluminum substrate which has undergone chemical etching with an alkaline etchant composition and deoxidation using a deoxidation solution having 50 vol % HNO_3. FIG. 3 shows a representative example of an aluminum substrate which has undergone chemical etching with an acid pickle composition and deoxidation using a deoxidation solution having a chromated deoxidizing component.

Electrolytic coating

[0043] The deoxidized aluminum substrates were coated using an electrolytic coating process, wherein the deoxidized aluminum substrates were placed on a titanium alloy rack and immersed in SurTec 650 inorganic finishing solution. A suitable DC power supply was connected to the titanium alloy rack and two 1000-series aluminum counter electrodes. The power supply was then operated to supply a constant voltage to provide a cathodic or anodic current density not exceeding 1.0 mA/cm^2. The duration of coating formation was equal to or less than 10 minutes, at which point the power supply was turned off, and the coated aluminum substrates were removed from the inorganic finishing solution. The coated aluminum substrates were then rinsed and dried.

Salt fog testing

[0044] Coating performance was evaluated in accordance with the neutral salt fog test outlined in ASTM B117. The coating applied to the aluminum metal substrate was determined to a MIL-A-8625 pass rating if in a neutral salt fog environment, at a minimum of 336 hours, there exists no formation of pits having a diameter greater than 0.031 in, no formation of more than 5 pits in a 30 in^2 area, and no formation of more than 15 pits in a 150 in^2 area. Herein, pits are defined as visible black colored spots or pits exhibiting white corrosion product surrounding the pit, or in the form of a tail. FIG. **4** and FIG. **5** show 7075-T6, and 2024-T3 aluminum metal substrates, which have undergone chemical etching with an alkaline etchant composition, deoxidation using a deoxidation solution having 50 vol % HNO_3, and electrolytically coated with an inorganic finish, after 336 hours within a neutral salt fog environment.

[0045] The phrases, unless otherwise specified, "consists essentially of" and "consisting essentially of" do not exclude the presence of other steps, elements, or materials, whether or not, specifically mentioned in this specification, so long as such steps, elements, or materials, do not affect the basic and novel characteristics of the present disclosure, additionally, they do not exclude impurities and variances normally associated with the elements and materials used.

[0046] Numerical ranges used herein include the numbers recited in the range. For example, the numerical range "from 1 wt % to 10 wt %" includes 1 wt % and 10 wt % within the recited range.

[0047] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited. Additionally, within a range includes every point or individual value between its end points even though not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[0048] All numerical values within the detailed description herein are modified by "about" the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

[0049] All documents described herein are incorporated by reference herein, including any priority documents and or testing procedures to the extent they are not inconsistent with this text. As is apparent from the foregoing general description and the specific aspects, while forms of the present disclosure have been illustrated and described, various modifications can be made without departing from the scope of the present disclosure. Accordingly, it is not intended that the present disclosure be limited thereby. Likewise, the term "comprising" is considered synonymous with the term "including" for purposes of United States law. Likewise whenever a composition, an element or a group of elements is preceded with the transitional phrase "comprising," it is understood that we also contemplate the same composition or group of elements with transitional phrases "consisting essentially of," "consisting of," "selected from the group of consisting of," or "is" preceding the recitation of the composition, element, or elements and vice versa.

[0050] While the present disclosure has been described with respect to a number of aspects and examples, those skilled in the art, having benefit of this disclosure, will appreciate that other aspects can be devised which do not depart from the scope of the present disclosure.

Claims

1. A method comprising:

(I) degreasing a metal substrate;

performing a first alkaline cleaning on the

metal substrate;
etching the metal substrate with an alkaline etchant solution to form an etched metal substrate, wherein the etched metal substrate comprises an average surface roughness (R_a) of about 250 μin (6.4 μm) or less;
deoxidizing the etched metal substrate to form a processed metal substrate;
optionally performing a second alkaline cleaning on the processed metal substrate; and
depositing a coating onto the processed metal substrate to form a coated metal substrate; or

(II) degreasing a metal substrate;

performing a first alkaline cleaning on the metal substrate;
etching the metal substrate with an alkaline etchant solution to form an etched metal substrate, the alkaline etchant solution comprising about 2 vol % to about 6 vol % of triethanolamine, about 2 vol % to about 30 vol % of a sodium sulfide additive, about 10 vol % to about 40 vol % of 50% sodium hydroxide, about 75 g/L or less of dissolved metal content, and about 6 g/L or less of ethylenediaminetetraacidic acid (EDTA);
deoxidizing the etched metal substrate with a deoxidizing solution comprising about 40 vol % to about 60 vol % of nitric acid to form a processed metal substrate;
performing a second alkaline cleaning on the processed metal substrate; optionally performing alkaline etch cleaning with said alkaline etchant and deoxidizing solution comprising about 40 vol % to about 60 vol % of nitric acid, which may be used alone or in combination with iron based or chromated deoxidizing solutions to remove oxides if needed nitric acid deoxidizing solution alone or in combination with other deoxidizing solutions to remove oxides as needed;
depositing a coating onto the deoxidized metal substrate to form a coated metal substrate.

2. The method of claim 1, comprising said (I):

degreasing a metal substrate;
performing a first alkaline cleaning on the metal substrate;
etching the metal substrate with an alkaline etchant solution to form an etched metal substrate, wherein the etched metal substrate comprises an average surface roughness (R_a) of about 250 μin (6.4 μm) or less;
deoxidizing the etched metal substrate to form a processed metal substrate;
optionally performing a second alkaline cleaning on the processed metal substrate; and
depositing a coating onto the processed metal substrate to form a coated metal substrate.

3. The method of claim 2, wherein the alkaline etchant solution comprises about 2 vol % to about 6 vol % of triethanolamine, about 2 vol % to about 30 vol % of a sodium sulfide additive, about 10 vol % to about 40 vol % of 50% sodium hydroxide, about 75 g/L or less of dissolved metal content, and about 6 g/L or less of ethylenediaminetetraacidic acid (EDTA).

4. The method of claim 2 or 3, wherein the processed metal substrate comprises an average surface roughness R_a of about 8 μin (0.2 μm) to about 16 μin (0.4 μm).

5. The method of any one of claims 2-4, wherein the sum of the highest peak and lowest valley (R_t) of the surface of the processed metal substrate is about 158 μin (4 μm) to about 236 μin (6 μm).

6. The method of any one of claims 2-5, wherein deoxidizing the etched metal substrate comprises immersing the etched metal substrate within a deoxidizing solution comprising about 40 vol % to about 60 vol % of nitric acid.

7. The method of any one of claims 2-6, wherein depositing a coating onto the processed metal substrate comprises electrolytically depositing an inorganic finish thereon, the electrolytic deposition of the inorganic finish comprising:

attaching the processed metal substrate to a counter electrode,
electrically connecting the processed metal substrate to a power supply,
immersing the processed metal substrate within an inorganic finishing solution,
applying a current density to the processed metal substrate to form a coated metal substrate,
removing the coated metal substrate from the inorganic finishing solution, and
rinsing the coated metal substrate;
optionally wherein the current density is applied to the processed metal substrate for about 2 min to about 5 min.

8. The method of any one of claims 2-7, wherein the coating applied to the metal substrate provides corrosion protection in a salt fog environment of 336-hours minimum without pits having a diameter of about 0.031 in or less; fewer than 5-pits in 30-in^2 and fewer than 15-pits in an area of 150-in^2.

9. The method of claim 1, comprising said (II):

degreasing a metal substrate;
performing a first alkaline cleaning on the metal substrate;
etching the metal substrate with an alkaline etchant solution to form an etched metal substrate, the alkaline etchant solution comprising about 2 vol % to about 6 vol % of triethanolamine, about 2 vol % to about 30 vol % of a sodium sulfide additive, about 10 vol % to about 40 vol % of 50% sodium hydroxide, about 75 g/L or less of dissolved metal content, and about 6 g/L or less of ethylenediaminetetraacidic acid (EDTA);
deoxidizing the etched metal substrate with a deoxidizing solution comprising about 40 vol % to about 60 vol % of nitric acid to form a processed metal substrate;
performing a second alkaline cleaning on the processed metal substrate; optionally performing alkaline etch cleaning with said alkaline etchant and deoxidizing solution comprising about 40 vol % to about 60 vol % of nitric acid, which may be used alone or in combination with iron based or chromated deoxidizing solutions to remove oxides if needed nitric acid deoxidizing solution alone or in combination with other deoxidizing solutions to remove oxides as needed;
depositing a coating onto the deoxidized metal substrate to form a coated metal substrate.

10. The method of claim 9, wherein depositing a coating onto the processed metal substrate comprises electrolytically depositing an inorganic finish thereon, the electrolytic deposition of the inorganic finish comprising:

attaching the processed metal substrate to a counter electrode,
electrically connecting the processed metal substrate to a power supply,
immersing the processed metal substrate within an inorganic finish solution,
applying a current density to the processed metal substrate to form a coated metal substrate,
removing the coated metal substrate from the inorganic finishing solution, and
rinsing the coated metal substrate;
optionally wherein the current density is applied to the processed metal substrate for about 2 minutes to about 5 minutes.

11. The method of claim 9 or 10, wherein:

(a) the processed metal substrate comprises an R_a of about 8 μin (0.2 μm) to about 16 μin (0.4 μm); and/or
(b) the R_t of the surface of the processed metal substrate is about 158 μin (4 μm) to about 236 μin (6 μm).

12. The method of any one of claims 9-11, wherein the coating applied to the metal substrate provides corrosion protection in a salt fog environment of 336-hours minimum without pits having a diameter of about 0.031 in or less, fewer than 5-pits in 30-in^2, and fewer than 15-pits in an area of 150-in^2.

13. The method of claim 9, wherein depositing a coating onto the processed metal substrate comprises electrolytically depositing an inorganic finish thereon, the electrolytic deposition of the inorganic finish comprising:

attaching the processed metal substrate to two or more counter electrodes,
electrically connecting the processed metal substrate to a power supply,
immersing the processed metal substrate within an inorganic finishing solution,
applying a current density to the processed metal substrate to form a coated metal substrate, and
rinsing the coated metal substrate.

14. The method of claim 13, wherein:

(a) the current density applied to the processed metal substrate is about 0.2 mA/cm^2 to about 0.5 mA/cm^2;
(b) the current density is applied to the processed metal substrate for about 2 minutes to about 5 minutes; and/or
(c) the current density is applied to the processed metal substrate as a constant current.

15. A coated metal substrate, comprising:

an etched metal substrate, the etched metal substrate comprising a metal substrate having an average surface roughness of about 79 μin (2 μm) to about 8 μin (0.2 μm), wherein:
the average surface roughness of the metal substrate is the result of etching the metal substrate in an etching solution and deoxidizing the metal substrate in a deoxidation solution comprising about 40 vol % to about 60 vol % of nitric acid, and
an inorganic finish disposed over the etched metal substrate, wherein the conversion coating comprises a morphology substantially as shown in Figure 2.

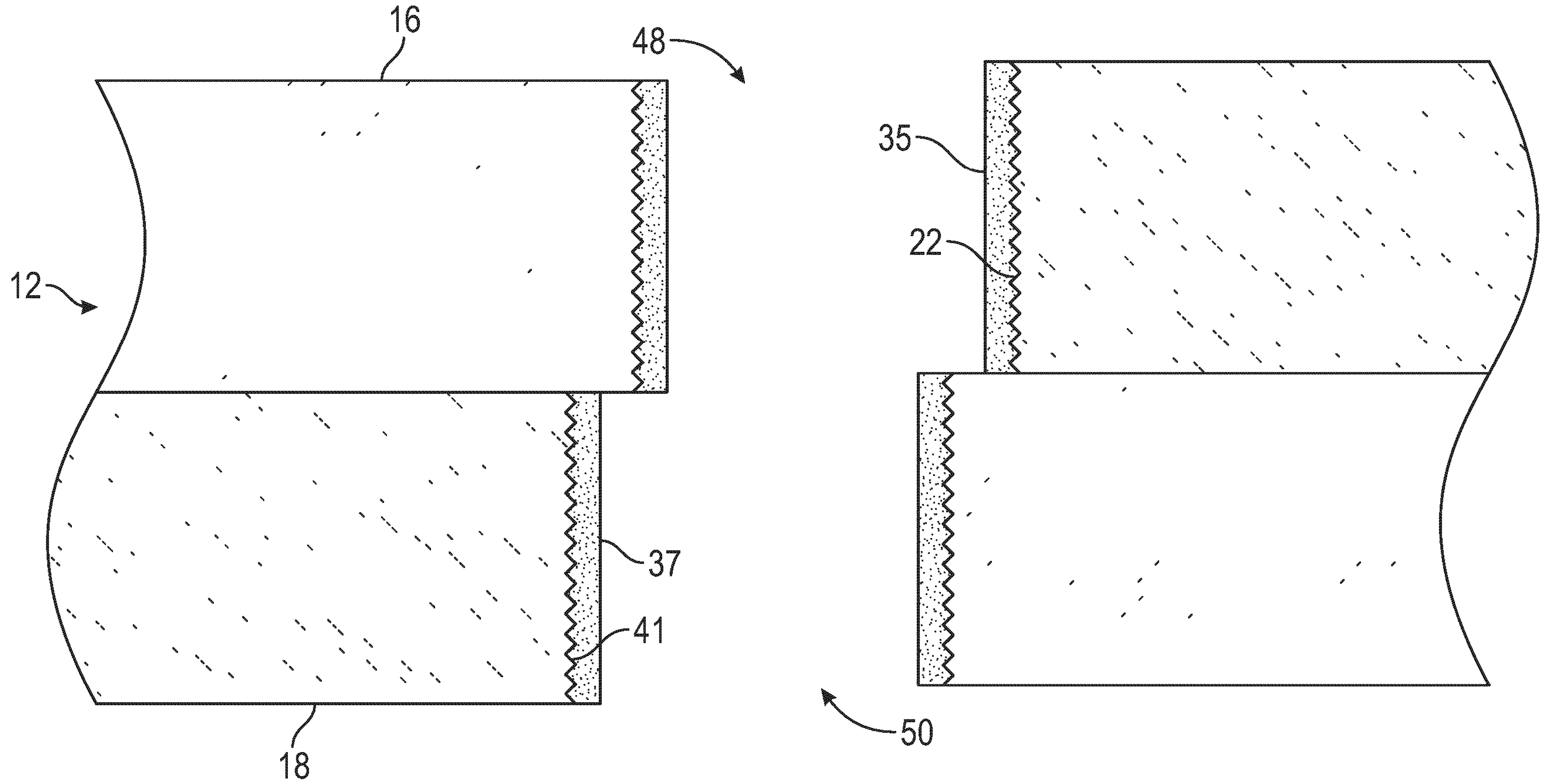

FIG. 1

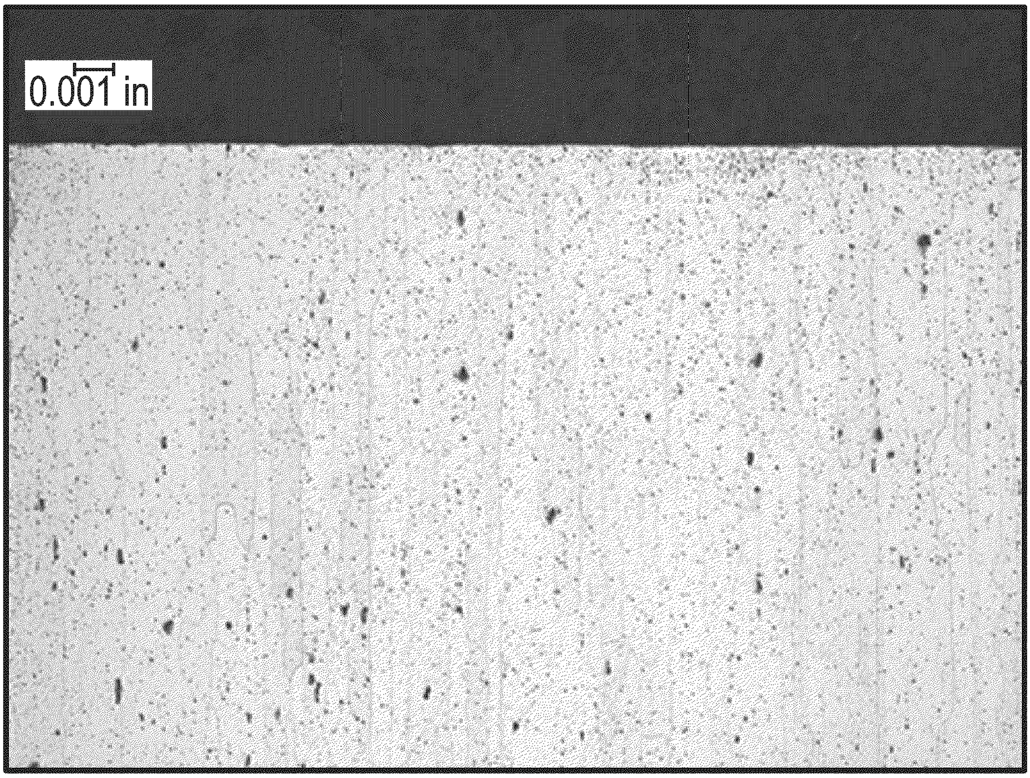

FIG. 2

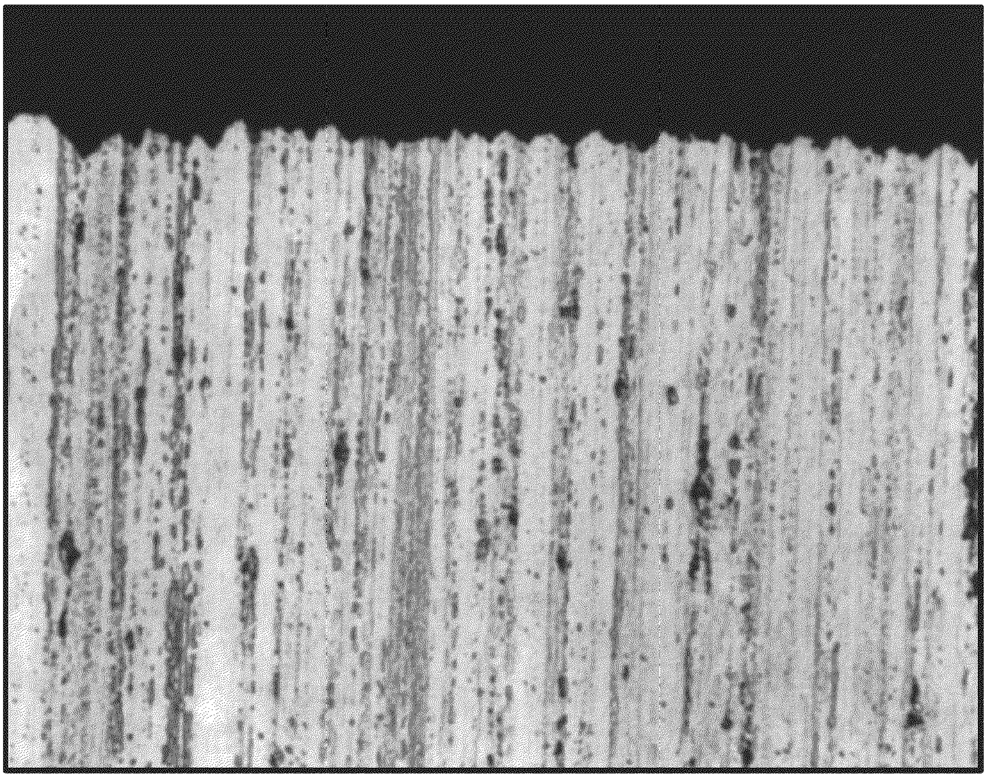

FIG. 3

FIG. 4

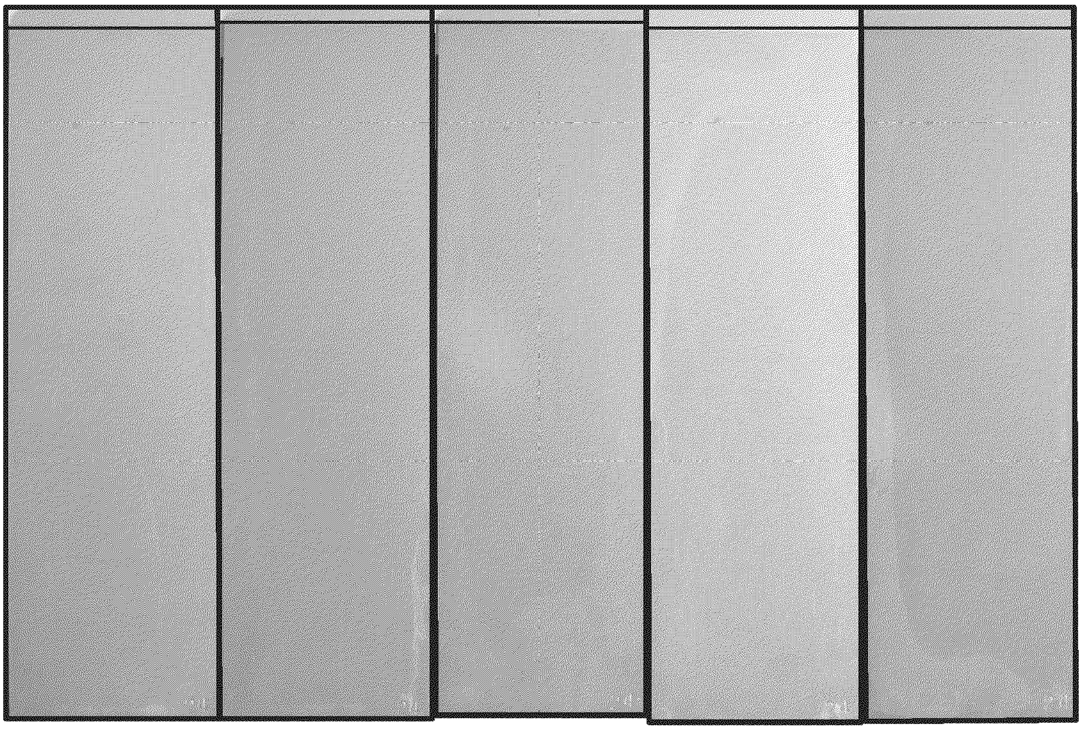

FIG. 5

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EUROPEAN SEARCH REPORT

Application Number
EP 24 18 8279

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CLASSIFICATION OF THE APPLICATION (IPC)
INV. C23F1/36 C23G1/12 C23G1/22 C25D11/38

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C23F C23G C23C C25D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	27 November 2024	Handrea-Haller, M

CATEGORY OF CITED DOCUMENTS

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