



(51) International Patent Classification:

C23C 22/34 (2006.01) C23C 22/44 (2006.01)
C23C 22/83 (2006.01)

(21) International Application Number:

PCT/US2015/064449

(22) International Filing Date:

8 December 2015 (08.12.2015)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/089,036 8 December 2014 (08.12.2014) US

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(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

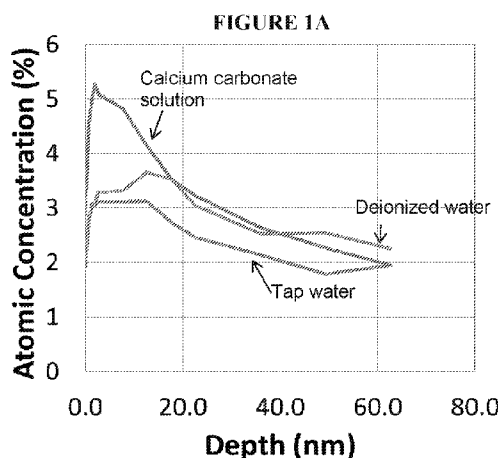
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
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SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments (Rule 48.2(h))

(54) Title: TREATMENT OF CONVERSION COATED METAL SURFACES WITH A CALCIUM-CONTAINING AQUEOUS AGENT



(57) Abstract: Described herein is a method for treating a metal surface, such as an aluminum alloy surface, which involves contact-
ing the surface coated with a pretreatment coating comprising fluoride ions with an aqueous agent comprising at least 7 ppm calcium
ions. The method reduces fluoride ion content in the pretreatment coating, increases calcium ion content in the pretreatment coating,
improves corrosion resistance, such as filiform corrosion resistance, of the metal surface, and/or improves adhesion between the sur-
face and a surface coating, such as a paint, lacquer, adhesive or a bonding agent. The aqueous agent can be a calcium-containing
rinse, for example, a solution of a calcium salt. Articles of manufacture comprising metal surfaces treated by the above methods as
well as the related manufacturing processes are also described.

TREATMENT OF CONVERSION COATED METAL SURFACES WITH A CALCIUM-CONTAINING AQUEOUS AGENT

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Provisional Application No. 62/089,036, filed
5 December 8, 2014, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

The present invention relates to the fields of material science, material chemistry,
surface chemistry, metal manufacturing, aluminum alloys, aluminum manufacturing and related
10 fields. The present invention provides novel compositions and processes for surface
pretreatment of metals, for example, aluminum alloys, in order to improve their corrosion
resistance. The compositions, processes and uses described herein can be employed in various
industries to produce articles or materials comprising metal surfaces, such as aluminum alloy
surfaces, including, but not limited to, motor vehicle parts or panels, construction or architectural
15 parts or panels, electronic housings, composite and bonded materials and articles, and other
products and parts comprising metal surfaces.

BACKGROUND

Articles manufactured from or including metals, such as aluminum alloys, often
20 contain surfaces covered with various types of films or coatings, for example, paints, lacquers or
bonding compounds, such as resins, glues or other types of adhesives. One problem associated
with the metal surfaces, such as aluminum alloy surfaces, covered with films or coatings is
filiform corrosion. The term “filiform corrosion” and other related terms typically refer to a type
of corrosion occurring at the interface between metal surfaces and thin films or coatings,
25 including organic and inorganic films and coatings. Filiform corrosion has an appearance of
randomly or semi-randomly distributed filaments emanating from one or more sources (“heads”)
under bulging and/or cracking coating. These filaments are channels or crevices comprised of
corrosion products, such as metal salts. Filiform corrosion is initiated by atmospheric water and
oxygen supplied to the initial site (which forms a “head”) by osmosis and propagates under the
30 film forming the filaments, which can be referred to as “tails.” Although the damage to a metal

surface caused by filiform corrosion may not be extensive, it detrimentally affects the coating, including its appearance, functional properties and bond with the surface. For example, filiform corrosion of a painted or aluminum alloy surface may lead to a surface riddled with channels filled with white aluminum hydroxide precipitate. In another example, filiform corrosion may lead to interfacial failure of a metal/adhesive or metal/bonding compound interface, which, in turn, may lead to a structural failure of an article containing such an interface. Filiform corrosion is associated with exposure to high humidity and also with the occurrence of various ions on the metal surface. A number of approaches have been employed to reduce filiform corrosion at a metal surface under a film or coating. One of these approaches is the use of the so-called pretreatment coatings or primers. Pretreatment coatings provide a stable metal oxide surface that resists filiform corrosion and promotes adhesion of the film or coating to the aluminum alloy surface. One class of pretreatment coatings are pretreatment coatings containing combinations of metal ions, such as Ti/Zr pretreatment coatings, which tie up oxygen at the metal surface in stable oxides that function as an oxygen diffusion barrier.

The formation of Ti/Zr pretreatment involves the hydrolysis of hexafluorotitanate and hexafluorozirconate to form Ti/Zr oxides, which produces free fluoride ions as a byproduct. Although the oxide layer provides a degree of protection from filiform corrosion and improves the bonding between the aluminum alloy surface and the coating, it is believed that the byproduct-free (non-complexed with Ti, Zr or other metal) fluoride ions lead to filiform corrosion propagation. The fluoride ions can easily incorporate into the Al oxide layers between the pretreatment coating and the alloy substrate and replace the oxygen in the Al oxide matrix, which eventually causes the dissolution of Al and leads to the corrosion of the alloy surface.

In an attempt to reduce free fluoride ion content, the pretreatment coating is typically rinsed after application with deionized water. This method requires large amounts of deionized water to lower fluoride ion levels. Production of the deionized water and treatment of the spent rinse solution to remove dissolved compounds prior to discharge both add to the costs of the above process and may create significant amounts of hazardous waste. More generally, improved bonding between aluminum alloy surfaces and various coatings would be beneficial for various industries and fields. Accordingly, improved processes and compositions for pretreatment of aluminum alloy surfaces are desired.

SUMMARY

The terms “invention,” “the invention,” “this invention” and “the present invention,” as used herein, are intended to refer broadly to all of the subject matter of this patent application and the claims below. Statements containing these terms should be understood not to limit the subject matter described herein or to limit the meaning or scope of the patent claims below. Covered embodiments of the invention are defined by the claims, not this summary. This summary is a high-level overview of various aspects of the invention and introduces some of the concepts that are further described in the Detailed Description section below. This summary is not intended to identify key or essential features of the claimed subject matter, nor is it intended to be used in isolation to determine the scope of the claimed subject matter. The subject matter should be understood by reference to appropriate portions of the entire specification, any or all drawings and each claim.

The present invention provides solutions to problems associated with filiform corrosion of metal surfaces, such as aluminum alloy surfaces, surfaces covered with organic or inorganic films or coatings, and, more generally, with the adhesion of coatings or films (for example, paint or adhesive adhesion). The present invention may be used to improve the adhesion between metal surfaces, such as aluminum alloy surfaces, and the films or coatings. It may also be used to improve adhesion between metal surfaces and other metal or non-metal surfaces bonded or glued together with bonding compounds or adhesives. The present invention addresses these problems by providing anti-corrosion pretreatment on a metal surface, such as an aluminum alloy surface, in which a pretreatment coating containing metal and fluoride ions, such as a Ti/Zr pretreatment coating, after its application to the metal surface, such as the aluminum alloy surface, is contacted with an aqueous agent containing calcium ions. The presence of free fluoride ions causes the corrosion of the metal surface which eventually leads to coatings detachment or bonding failure. Calcium ions in the aqueous agent form ionic bonds with free fluoride ions in the pretreatment coating. It is understood that, as a result of the ionic attraction, fluoride ions leach out of the pretreatment coating, which simplifies their removal from the pretreatment coating, for example, by rinsing the pretreated surface. Furthermore, it is also understood that calcium ions from the calcium-containing aqueous agent migrate into the Ti/Zr coating layer, and ionic bonds are formed between calcium and fluoride ions remaining in the

coating layer. Thus formed CaF_2 is insoluble, which is a reason calcium ions can be employed to stabilize the free fluoride ions. This phenomenon sequesters fluoride ions in insoluble complexes, thus lowering their availability for filiform corrosion propagation. These phenomena, which are described according to current understanding and are not intended to limit the present invention, as well as other phenomena, some of which are discussed further herein, reduce the propensity of the aluminum alloy surface for filiform corrosion and improve the bonding between the surface and the coatings or films. Although differences may exist in the adhesion of surface coatings to metal surfaces, such as cosmetic paints, and adhesion of compounds use for structural bonding (for example, adhesives), the present invention may be used to improve adhesion of both surface coatings and adhesion of bonding compounds.

The improved processes described herein can possess various advantages. For example, they can be less costly than conventional pretreatments, use less water, and produce less hazardous waste than the conventional pretreatments, such as those employing deionized water rinses. Some embodiments of the present invention are processes for anti-corrosion pretreatment of aluminum alloys that utilize calcium-containing aqueous agents. Compositions of matter related to calcium-containing aqueous agents as well as uses of a calcium-containing aqueous agent in the process of anticorrosion pretreatment are also included within the embodiments of the present invention. Some other embodiments of the present invention are processes of producing or manufacturing articles that comprise coated aluminum alloy surfaces treated by the improved surface pretreatment. The present invention also encompasses articles manufactured according to the above processes, including materials containing aluminum alloy surfaces. Some exemplary embodiments of the present invention are summarized below.

One exemplary embodiment of the present invention is a method for treating a metal surface coated with a pretreatment coating comprising fluoride ions. The method includes a step of contacting the metal surface one or more times with an aqueous agent comprising at least 7 ppm calcium ions. Another exemplary embodiment of the present invention is a method for pretreatment of a metal surface, which includes the steps of: coating the metal surface with a pretreatment coating; and, contacting the metal surface coated with the pretreatment coating with an aqueous agent comprising at least 7 ppm calcium ions. One more exemplary embodiment of the present invention is a method of improving corrosion resistance of a metal surface, which

includes the steps of coating the metal surface with a pretreatment coating and contacting the metal surface coated with the pretreatment coating with an aqueous agent comprising at least 7 ppm calcium ions. In the embodiments of the present invention, the metal surface can be an aluminum alloy surface, for example, a surface of a 2xxx, 3xxx, 5xxx, 6xxx or 7xxx aluminum alloy. In the embodiments of the present invention, the pretreatment coating can be a Ti/Zr or Zr/Cr coating. For example, the pretreatment coating can be hexafluorotitanate, hexafluorozirconate or chromium sulfate coating. According to the embodiments of the present invention, the aqueous agent can be a solution of a calcium salt, for example, a calcium carbonate, a calcium phosphate, a calcium nitrate or a calcium sulfate. The aqueous agent can contain calcium (Ca^{2+}) ions in an amount of at least about 7 ppm (about 7 ppm or above), for example, at least about 7.5 ppm, at least about 8.0 ppm, at least about 8.5 ppm, at least about 9 ppm, or at least about 9.5 ppm. In some embodiments, the aqueous agent can contain calcium ions in an amount of from about 7.5 ppm to about 500 ppm, (e.g., from about 8 ppm to about 450 ppm, from about 8.5 ppm to about 400 ppm, from about 9.0 ppm to about 350 ppm, from about 9.5 ppm to about 300 ppm, from about 10 ppm to about 250 ppm, from about 20 ppm to about 200 ppm, from about 50 ppm to about 100 ppm, or from about 10 ppm to about 50 ppm). In some embodiments, the aqueous agent can contain calcium ions in a range of from about 7.5-9.8 ppm. In some embodiments, the aqueous agent can contain calcium ions at about 7.5 ppm. In some other embodiments, the aqueous agent can contain calcium ions at saturation. In some exemplary embodiments, the aqueous agent is a saturated solution of calcium carbonate.

The step of contacting the metal surface with the aqueous agent in the processes according to the embodiments of the present invention can include one or more of immersing the metal surface in the agent, rinsing the metal surface with the agent, rolling the agent onto the metal surface, or spraying the metal surface with the agent. After the step of contacting the metal surface with the aqueous agent according to the embodiments of the present invention, the fluoride ion content can be reduced in the pretreatment coating, and/or calcium ion content can be increased in the pretreatment coating. In some embodiments, the metal surface is rinsed with the aqueous agent in the contacting step, and the weight of the pretreatment coating after the contacting step is greater in comparison to a metal surface coated with the pretreatment coating rinsed with deionized water. The embodiments of the present invention can include, after the

contacting step, a step of applying to the metal surface one or more of a paint, a lacquer, an adhesive, a glue or a bonding compound.

The embodiments of the present invention include articles of manufacture comprising a metal surface treated by the methods according to the embodiments of the present invention.

5 Some examples of such articles of manufacture are an aluminum alloy sheet, a motor vehicle panel, an automotive panel, an electronics panel, an architectural panel or a material comprising an aluminum alloy surface. Processes of manufacturing the articles of manufacture which include the methods according to the embodiments of the present invention are also encompassed by the embodiments of the present invention. Other embodiments, objects and
10 advantages of the present invention will be apparent from the following detailed description of embodiments of the invention.

BRIEF DESCRIPTION OF THE FIGURES

FIGURE 1A shows a line plot illustrating depth profiling x-ray photoelectron spectroscopy (XPS) data for Ti after rinsing pretreated aluminum alloy samples with deionized
15 water, tap water and calcium carbonate solution.

FIGURE 1B shows a line plot illustrating depth profiling x-ray photoelectron spectroscopy (XPS) data for Zr after rinsing pretreated aluminum alloy samples with deionized water, tap water and calcium carbonate solution.

FIGURE 2A shows a line plot illustrating depth profiling XPS data for Si after rinsing
20 pretreated aluminum alloy samples with deionized water, tap water and calcium carbonate solution.

FIGURE 2B shows a line plot illustrating depth profiling XPS data for O after rinsing pretreated aluminum alloy samples with deionized water, tap water and calcium carbonate solution.

25 FIGURE 3A shows a line plot illustrating depth profiling XPS data for Ca after rinsing pretreated aluminum alloy samples with deionized water, tap water and calcium carbonate solution.

FIGURE 3B shows a line plot illustrating depth profiling XPS data for F after rinsing pretreated aluminum alloy samples with deionized water, tap water and calcium carbonate solution.

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DETAILED DESCRIPTION

Described herein are pretreatment compositions and improved methods of pretreating aluminum alloy surfaces, which also can be applied to the pretreatment of other metal surfaces. The improved pretreatment lowers the concentration of free fluoride ions at the surface of a metal, such as an aluminum alloy surface, coated with the pretreatment coating, as well as in the pretreatment coating. By reducing the content of free fluoride ions, the improved pretreatment reduces and/or inhibits propagation of filiform corrosion on a metal surface. By reducing the filiform corrosion, the improved anticorrosion pretreatment generally improves the bond between a film or coating (for example, paint or adhesive) and the metal surface. In some exemplary embodiments, the improved anticorrosion pretreatment leads to improved bond durability when adhesive compounds are used to bond metal surfaces with other metal or non-metal surfaces. In some other exemplary embodiments, the improved anticorrosion pretreatment leads to more durable and stable bonds between a metal surface and a coating applied on the metal surface, such as a coating or paint. The embodiments of the present invention include methods for treating metal surfaces, such as aluminum alloy surfaces. The methods are performed with the goal of inhibiting corrosion, such as filiform corrosion, of the metal surfaces, such as aluminum alloy surfaces, covered with an organic or inorganic coating or film, including protective and/or decorative coatings, such as lacquers or paints, adhesive or bonding compounds, such as glues or resins, or other types of films, coatings or compounds. The methods of the present invention can therefore be referred to as anticorrosion pretreatment or methods to improve corrosion resistance or other related terms.

The methods according to some embodiments of the present invention can also be described as surface pretreatment methods, methods of treating aluminum alloy surfaces, methods of treating metal surfaces or other related terms. The methods of the invention

comprise one or more steps of contacting a metal surface, such as an aluminum alloy surface, which has been treated by a pretreatment agent comprising metal ions and fluoride ions, such as Zr, Ti, Cr, Ce, or V-based agents, with an aqueous agent comprising calcium ions (Ca^{2+}). The aqueous agent used in the methods of the present invention may contain at least 7 ppm Ca^{2+} ions in an aqueous solution, and can be referred to as a calcium-containing agent. As discussed above, the exposure of the pretreatment coating layer to the calcium-containing agent leads to formation of ionic bonds between calcium ions originating in the calcium-containing agent and free fluoride ions (F^-) found in the pretreatment coating layer. Due to the ionic attraction to calcium ions, fluoride ions leach out to the surface of the pretreatment coating, while calcium ions from the agent migrate into the pretreatment coating layer, sequestering fluoride ions remaining in the layer in ionic complexes, such as CaF_2 complexes, which are poorly soluble. The amount of free fluoride ions found in the pretreatment coating layer is thereby reduced, which alleviates filiform corrosion propagation under the film coating applied onto the metal surface. Additional phenomena may be involved, which also inhibit filiform corrosion. For example, the presence of calcium ions at the metal surface may increase the pH at the surface. Higher pH, particularly in the alkaline range, inhibits propagation of filiform corrosion.

The phenomenon of filiform corrosion described above is intended to aid in the description and the understanding of the embodiments of the present invention. While the pretreatment processes according to the embodiments of the present invention may alleviate filiform corrosion, the advantages of using the methods of the present invention are not limited to reducing, inhibiting, or alleviating filiform corrosion or its propagation. Based on the experimental data, a contact with a calcium-containing agent may increase the weight of the pretreatment coat on a metal surface, improving bond durability with the final coating. More generally, the pretreatment processes according to the embodiments of the present invention improve durability of the coatings applied onto metal surfaces and/or improve durability between the coating and the metal surface. The pretreatment processes according to the embodiments of the present invention also improve the stability of the interface between a metal surface and an organic or inorganic film or coating applied onto it and/or improve the bond between metal surfaces and other metal or non-metal components bonded to such surfaces with bonding compounds or adhesives, which leads to reduced failure of the above interfaces. Furthermore,

the pretreatment processes according to the embodiments of the present invention improve adhesion between a film or coating and a metal surface, and reduce the possibility of adhesion failure between metal surfaces and other metal or non-metal components bonded to them with bonding or adhesive compounds metal or non-metal surfaces.

5 The metal surfaces suitable for pretreatment according to the embodiments of the present invention include surfaces of various alloyed and non-alloyed metals, for example, iron, magnesium, zinc, copper, brass and aluminum and their alloys. The aluminum alloy surfaces suitable for pretreatment according to the embodiments of the present invention include surfaces comprised of aluminum alloyed with various elements, such as Fe, Mn, Si, Mg, Cu, etc. as well
10 as surfaces comprised of substantially pure aluminum. In other words, the term “aluminum alloy surface” is not intended to be limited by the type of an aluminum, alloyed or unalloyed. Some examples of aluminum alloys suitable for the pretreatment according to the embodiments of the present invention are 2xxx, 3xxx, 5xxx, 6xxx or 7xxx aluminum alloys (according to Aluminum Association (AA) Designation). The term “surface” as used herein generally means an outer part
15 of a quantity of a metal, such as an aluminum alloy. In some cases, a surface may be an outer part when subjected to the pretreatment, but later may be on the inside of an object or a material. For example, a multilayer composite comprising one or more metal layers may contain, on the inside, surfaces treated according to the processes of the present invention and subsequently bonded with other metal or non-metal surfaces.

20 As discussed above, the methods according to some embodiments of the present invention involve a metal surface, such as an aluminum alloy surface, that has been subjected to pretreatment coating (“pretreated”) with a pretreatment coating or agent comprising metal ions and fluoride ions. The description of pretreatment coatings provided above is intended to aid in the understanding of the present invention. Examples of pretreatment coatings comprising metal
25 ions and fluoride ions include Ti/Zr and Zr/Cr coatings. Some other non-limiting examples of the pretreatment coatings are hexafluorotitanate, hexafluorozirconate and chromium sulfate coatings, conversion coatings based on chromium (chromium sulfate or chromate - Cr(VI) – e.g., K_2CrO_4), cerium (cerium chloride/hydroxide, cerium nitrate) coatings, vanadate (vanadate sulfate) coatings, or manganese (for example, manganese phosphate) coatings.

Pretreatment coatings are applied to aluminum alloy surfaces using appropriate processes, such as etching, pretreating, rinsing, and curing. A pretreatment coatings may be characterized by the content of constituent elements, such as Ti, Zr, etc. Pretreatment coating forms a pretreatment film upon application, but the terms “coating” and “film” can be used interchangeably in this context. A pretreatment coating can be characterized by a thickness of the film formed by the pretreatment coating, for example, it can be about 20 nm to about 10 μ m thick (e.g., about 25 nm to about 8 μ m, about 50 nm to about 6 μ m, about 75 nm to about 4 μ m, about 100 nm to about 2 μ m, about 125 nm to about 1 μ m, about 150 nm to about 800 nm, about 175 nm to about 600 nm, about 200 nm to about 575 nm, about 225 to about 550 nm, about 250 nm to about 500 nm, about 275 nm to about 475 nm, about 300 nm to about 450 nm, about 325 nm to about 425 nm, or about 350 nm to about 400 nm). For example, the film formed by the pretreatment coating can be about 20 nm, about 30 nm, about 40 nm, about 50 nm, about 60 nm, about 70 nm, about 80 nm, about 90 nm, about 100 nm, about 200 nm, about 300 nm, about 400 nm, about 500 nm, about 600 nm, about 700 nm, about 800 nm, about 900 nm, about 1 μ m, about 2 μ m, about 3 μ m, about 4 μ m, about 5 μ m, about 6 μ m, about 7 μ m, about 8 μ m, about 9 μ m, or about 10 μ m. The processes of the present invention may improve the performance of the pretreatment coating, for example, by (1) reducing free fluoride ion content in the film (2) stabilizing the free fluoride ions remaining in the coating and (3) increasing the coat weight constituent elements in the film, for example, Ti and Zr. When subjected to the processes according to the embodiments of the present invention, the pretreatment coating on an aluminum alloy surface may contain detectable levels of calcium, for example 7–500 ppm or 10–50 ppm. It is to be understood that one or more steps (e.g., two or more steps, three or more steps, four or more steps, etc.) of applying a pretreatment coating may be included in the processes of the present invention, and that one or more types of pretreatment coating (e.g., two or more types of pretreatment coating, three or more types of pretreatment coating, four or more types of pretreatment coating, etc.) may be employed.

As discussed above, the processes according to the embodiments of the present invention involve one or more steps of contacting the aluminum alloy surface coated with a pretreatment coating with an aqueous calcium-containing agent. An aqueous calcium-containing agent contains calcium (Ca^{2+}) ions in an amount of at least about 7 ppm (7 ppm or above, which can

also be expressed as ≥ 7 ppm), for example, at least about 7.5 ppm, at least about 8.0 ppm, at least about 8.5 ppm, at least about 9 ppm, or at least about 9.5 ppm. In some embodiments, the aqueous agent can contain calcium ions in an amount of from about 7.5 ppm to about 500 ppm, from example, from about 8 ppm to about 450 ppm, from about 8.5 ppm to about 400 ppm, from about 9.0 ppm to about 350 ppm, from about 9.5 ppm to about 300 ppm, from about 10 ppm to about 250 ppm, from about 20 ppm to about 200 ppm, from about 50 ppm to about 100 ppm, or from about 10 ppm to about 50 ppm. In some embodiments, the aqueous agent can contain calcium ions in a range of from about 7.5-9.8 ppm. In some embodiments, the aqueous calcium-containing agent can contain calcium ions at about 7.5 ppm. In some embodiments, an aqueous calcium-containing agent contains calcium ions at saturation.

Examples of aqueous agents include an aqueous solution, a sol, or a gel. An aqueous agent used in the pretreatment methods of the present invention may contain calcium salts, such as calcium carbonate, calcium nitrate, calcium sulfate, calcium phosphate, etc. In addition to calcium ions and/or salts, an aqueous agent may contain other metal ions or salts, as well as other components. One example of an aqueous agent is a saturated solution of a calcium salt, such as CaCO_3 . Another example is an aqueous solution containing calcium ions and detectable levels of one or more of Al, Mg, Si, and Mn. Embodiments of the present invention encompass aqueous agents described herein as well as their uses in the processes of the present invention.

Various suitable methods may be employed in the processes of the present invention for contacting a calcium-containing aqueous agent with a pretreated metal surface, such as an aluminum alloy surface. Bringing the metal surface, such as the aluminum alloy surface, and the calcium-containing aqueous agent into contact may also be described as exposing the surface to the aqueous agent, or applying the aqueous agent. Examples of methods that may be used to bring the metal surface, such as the aluminum alloy surface, and the calcium-containing agent into contact include, but are not limited to, immersing (for example, by immersion of the surface into a bath or other type of vessel containing the calcium-containing agent), rinsing or spraying, or rolling the agent onto the surface. Suitable methods and conditions are selected and optimized based on various considerations, such as the desired extent of calcium penetration into the pretreatment coating, the extent of fluoride ion reduction in the pretreatment coating, the type of the agent used and/or the type of the surface being treated. The ease of integrating the

pretreatment processes of the present invention into the manufacturing processes and lines is also taken into account. One or more contacting steps may be employed. For example, one, two, three, four, five or more steps are possible. In some embodiments of the processes according to the present invention, more than one step of applying a pretreatment coating may be included, in which case, a calcium-containing agent may be applied one or more times after each step of the pretreatment coating or after some (one or more) of the steps. Contact of the pretreated aluminum alloy surface with the calcium-containing agent may be conducted at various temperatures, for example at a temperature from approximately 15°C to 85°C. The duration of the contact of the pretreated metal surface, such as the pretreated aluminum alloy surface, with the calcium-containing agent may also vary. In some embodiments, the contact duration can range from several seconds (e.g., two or more seconds, three or more seconds, four or more seconds, five or more seconds, six or more seconds, seven or more seconds, eight or more seconds, nine or more seconds, 10 or more seconds, 15 or more seconds, 20 or more seconds, 25 or more seconds, or 30 or more seconds) to one or more minutes (e.g., two or more minutes, three or more minutes, four or more minutes, five or more minutes, six or more minutes, seven or more minutes, eight or more minutes, nine or more minutes, 10 or more minutes, 11 or more minutes, 12 or more minutes, 13 or more minutes, 14 or more minutes, 15 or more minutes, 16 or more minutes, 17 or more minutes, 18 or more minutes, 19 or more minutes, or 20 or more minutes). For example, the duration of the contact of the pretreated metal surface with the calcium-containing agent can range from about 2 seconds to 20 minutes, from about 10 seconds to about 15 minutes, from about 30 seconds to about 10 minutes, or from about 1 minute to 5 minutes. The selected duration, which may also be referred to as “dwell time,” may depend on various factors, such as the type of the pretreatment coating, concentration of the pretreatment agent or the method of application.

After the step of contacting the pretreated metal article, such as an aluminum alloy article, with the calcium-containing aqueous agent, the processes of the present invention may further contain one or more steps (two or more, three or more, four or more, etc.) of applying one or more films or coatings. The embodiments of the present invention are applicable to either organic and inorganic films or coatings. Some non-limiting examples of inorganic coatings are zinc phosphate, zirconium oxide, and E-coat. Some non-limiting examples of organic coatings

are films (such as protective or decorative films), paints, lacquers, adhesives, bonding compounds, glues and resins, or primers. It is to be understood that more than one type of coating (e.g., one or more, two or more, three or more, etc.) may be employed.

Embodiments of the present invention include processes of producing or manufacturing articles that comprise coated metal surface(s), such as aluminum alloy surface(s), treated by the surface pretreatment processes discussed above. The processes may be employed in various industries, including motor vehicle, aircraft or electronics manufacturing, automotive industry, transportation industry, or more generally, in any industry where adhesive bonds of metal parts, such as aluminum alloy parts, are used.

The present invention also encompasses articles and materials manufactured by the above processes described herein. Examples of the articles include motor vehicle parts or panels, ship or aircraft parts or panels, construction or architectural parts or panels and electronic housing parts. Other examples of materials include composite and bonded materials, including metals, such as aluminum alloys, layered composites or laminates including aluminum layers adhered or bonded to aluminum or other types of layers, and clad or monolithic aluminum alloy sheets, such as those containing, for example, 2xxx, 3xxx, 5xxx, 6xxx and 7xxx aluminum alloys. More generally, the present invention encompasses articles and materials that are manufactured by the processes described herein and include coated or bonded metal surfaces, such as aluminum alloy surfaces, or articles and other products or parts comprising coated or bonded metal surfaces, such as aluminum alloy surfaces.

Advantages afforded by the embodiments of the present invention include those discussed above. Further advantages of the embodiments of the present invention include improved methods producing a coated metal article, such as an aluminum article, with at least the same durability and corrosion resistance as the conventional processes, while reducing the costs and the hazardous waste. In one example, when rinsing a pretreated aluminum surface with a calcium-containing solution instead of rinsing with deionized water, a significant reduction of water usage may be achieved, because less rinsing agent is required to achieve at least a comparable reduction in fluoride levels. In another example, tap water may be employed as a calcium-containing rinse agent.

The following examples will serve to further illustrate the present invention without, at the same time, however, constituting any limitation thereof. On the contrary, it is to be clearly understood that resort may be had to various embodiments, modifications and equivalents thereof which, after reading the description herein, may suggest themselves to those skilled in the art without departing from the spirit of the invention.

EXAMPLES

Example 1

Aluminum alloys pretreated with Ti/Zr-based pretreatment film

An experimental study was conducted to test a hypothesis that Ca^{2+} ions in rinsing tap water form ionic bonds with the excessive F^- ions present in a Ti/Zr-based pretreatment film. If this phenomenon takes place, it may stabilize F^- ions and reduce the possibility of corrosion and adhesion failure of the pretreatment film. The study was conducted using samples of AA5754 and AA6111 aluminum alloys. Three types of rinses were tested, including deionized (DI) water, tap water, and an artificially prepared calcium-containing rinse ("calcium rinse"). The calcium rinse was a saturated solution of CaCO_3 in deionized water at 65°C . The CaCO_3 rinse was prepared by adding CaCO_3 to DI water to a saturation level and then purging the resulting solution with CO_2 . The results of inductively coupled plasma (ICP) analysis of different rinses are shown in Table 1. In particular, the concentration of calcium CaCO_3 rinse was determined to be about 15 ppm. The concentration of calcium in tap water was determined to be about 7.5-9.8 ppm (see Table 1).

TABLE 1

ICP of calcium-containing rinses

Final rinse	ICP results in ppm					
	Ca	Mg	Na	Si	S	Fe
DI	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Tap	7.5-9.8	1.9	7.1	3.0	5.4	<0.1

Ca	Saturated	<0.1	<0.1	<0.1	<0.1	<0.1
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The aluminum alloy samples were prepared as follows. Mill-finished AA5754 and AA6111 samples were subjected to the following sequential steps: (1) acidic etching in a solution of ferric sulfate and sulfuric acid, (7%) at 40-80 °C for 5-30 seconds; (2) rinsing in DI water at 65 °C for 8 seconds; (3) pretreatment in the pretreatment solution at 40-80° C for 4-30 seconds; (4) air drying for 5-30 seconds at room temperature; (5) final rinsing by immersing each sample in one of the three different rinses at 40-80 °C for 4-30 seconds; and (6) air drying with clean compressed air. The titanium coat weight for each sample was determined by X-ray fluorescence (XRF). A description of XRF analysis protocol is provided, for example, in “S2 Ranger. Spectrometry Solutions.” published in 2013 by Bruker AXS (Germany). The results of the XRF analysis are summarized in Table 2.

TABLE 2
Ti coat weight determination

Final rinse	Ti coat weight (mg/m ²)	
	AA5754	AA6111
DI	9.5	11.5
Tap	9.1	9.4
Ca	11.0	13.4

It was determined that the relative Ti coat weight was greater for AA6111 samples than for AA5754 samples. For both alloys, the relative Ti coat weights increased in the following sequence of rinses: tap water rinse < DI water rinse < calcium-containing rinse.

Elemental depth profiling of AA6111 alloy samples was performed using x-ray photoelectron spectrometry (XPS). A description of XPS protocols is provided, for example, in “Axis Ultra. Operators Manual” published in 1998 by Kratos Analytical (UK). The results are

illustrated in Figures 1A, 1B, 2A, 2B, 3A, and 3B. As illustrated in Figures 1A and 1B, the greatest signal for Ti and Zr at the Ti/Zr-pretreated sample surface was registered after the calcium rinse, which is consistent with greater coat weight registered with the XRF determination. As illustrated in Figures 2A and 2B, the samples rinsed with the calcium rinse also showed stronger signals of both Si and O, in comparison with DI-rinsed samples, which indicates that a greater pretreatment coat weight was present on the samples rinsed with the calcium rinse. As shown in Figures 3A and 3B, a much stronger signal of calcium was detected on the Ti/Zr-pretreated AA6111 after the calcium rinse than on the other two samples. No calcium was detected on the DI water-rinsed sample. As also illustrated by Figures 3A and 3B, for the DI water-rinsed sample, fluoride tended to be rinsed out of the coating and then enriched at the Ti/Zr surface; in contrast, fluoride in the sample rinsed with the calcium rinse was stable and distributed through the coating. The above results indicate that free fluoride in the Ti/Zr coating leached out from Ti/Zr coating into the calcium rinses, and that free F in the coating was sequestered in the film by calcium that migrated into the film from the rinse. The above results also indicate that a greater weight of the pretreatment coating was achieved by using calcium-containing rinses, signaling improved bonding between the pretreatment coating and the aluminum alloy surface.

The above results indicate that a calcium-containing rinse reduced free fluoride ion content in the pretreatment coating from approximately 7% (atomic concentration) to 5%, as illustrated by Figure 3B, and increased the coat weight of Ti (from an atomic concentration of 3% to 5%) and Zr (from an atomic concentration of 1% to 1.4%), as illustrated by Figure 1A and Figure 1B.

EXAMPLE 2

Effect of various rinses on a Ti/Zr-based pretreatment film

An experimental study of the effects of various rinses on a Ti/Zr-based pretreatment film was conducted. The study was conducted using samples of AA5754 and AA6111 aluminum alloys. Three types of rinses were tested, including deionized (DI) water, Georgia tap water, and artificially prepared calcium-containing rinses, which were prepared as solutions of $\text{Ca}(\text{HCO}_3)_2$, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, CaSO_4 , $\text{Ca}(\text{NO}_2)_2$ and $\text{Ca}(\text{NO}_3)_2$ in deionized water at 65°C. Each solution had a Ca^{2+} concentration of 200 ppm. Aluminum alloy samples were etched and pretreated as

described in Example 1, except for the final rinse step. Different rinses were used on the pretreated samples for the same periods of time. Titanium coat weight for each sample was determined by X-ray fluorescence (XRF) and the polymer coat weight was determined by UV-visible spectroscopy (UV/vis). The results of the XRF and UV/vis analysis are summarized in Table 3. For AA6111, the coat weights of both Ti and polymer showed a dependence on the type of calcium salt used in the rinse. The samples rinsed with $\text{Ca}(\text{HCO}_3)_2$ -based rinse showed the highest Ti coat weight but the lowest polymer weight, while the samples rinsed with $\text{Ca}(\text{NO}_3)_2$ -based rinse showed the lowest Ti weight, but the highest polymer weight.

Stress durability tests were conducted, and the results of these tests are also summarized in Table 3. Briefly, two aluminum alloy laps were bonded using the adhesive to form a joint. Six of these lap joints were connected by fasteners in a series and a tensile strength of 2400 ± 25 N was applied to the series of joints. The samples were exposed to a humid atmosphere ($\text{RH} > 90\%$) for 22 hours, immersed in a 5 wt. % solution of NaCl for 1 hour, and air-dried for 1 hour. The above treatment represents one cycle, and bond durability was determined by the number of cycles the samples pass before they break.

TABLE 3

Experimental results of the testing.

Final rinse	Stress testing results for joints 1-6							Ti coat weight (mg/m^2)	Polymer coat weight (mg/m^2)
	1 (top)	2	3	4	5	6 (bottom)	MCTF*		
$\text{Ca}(\text{CHO}_3)_2$	8	8	8	8	8	6	8	21.3	6.2
$\text{Ca}(\text{H}_2\text{PO}_4)_2$	25	25	25	25	25	25	25	16.2	6.5
CaSO_4	25	25	25	25	25	25	25	17.6	7.3
$\text{Ca}(\text{NO}_2)_2$	25	25	25	25	25	25	25	15.2	9.0
$\text{Ca}(\text{NO}_3)_2$	10	10	10	10	5	9	9	11.3	10.7
Georgia tap water	25	25	25	25	25	25	25	16.3	7.0
DI water	25	25	25	25	25	25	25	18.1	6.2

*MCTF = mean cycle to failure

Table 3 shows the dependence of the stress durability results for the AA6111 samples on the calcium-containing agents used in the final rinse step. The joints were in vertical position during the stress durability testing, and numbered 1 through 6, top to bottom. The samples
 5 rinsed with $\text{Ca}(\text{HCO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$ -based rinses failed after 8-10 cycles, while the rest of the samples passed 25 cycles. The stress durability testing showed that the choice of salt employed in the rinse solution influences bond durability.

EXAMPLE 3

A stress durability test was used to assess the effect of the pretreatment and adhesive on
 10 bond durability. The study was conducted using a sample of an AA6111 aluminum alloy including a Ti/Zr-based pretreatment film. The aluminum alloy samples were etched and pretreated as described in Example 1. Different rinses were used on the pretreated samples for rinse times of 10 seconds. Three types of rinses were tested, including deionized (DI) water, Georgia tap water, and artificially prepared calcium-containing rinses, which were prepared as
 15 solutions of $\text{Ca}(\text{HCO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, $\text{Ca}(\text{NO}_2)_2$, and CaSO_4 in deionized water at 65°C. Each solution had a Ca^{2+} concentration of 200 ppm.

In the stress durability test, a set of 6 lap joints/bonds were connected in sequence by bolts and positioned vertically in a 100% relative humidity (RH) humidity cabinet. The temperature was maintained at 50 ± 2 °C. A tensile load of 2.4 kN was applied to the bond
 20 sequence. The stress durability test is a cyclic exposure test that is conducted for up to 45 cycles. Each cycle lasts for 24 hours. In each cycle, the bonds are exposed in the humidity cabinet for 22 hours, then immersed in 5% NaCl for 15 minutes, and finally air-dried for 105 minutes. Upon the breaking of three joints, the test is discontinued for the particular set of joints. The completion of 45 cycles indicates that the set of joints passed the bond durability test.

25 The test results are shown below in Table 4. In Table 4, each of the joints are numbered 1 through 6, where joint 1 is the top joint and joint 6 is the bottom joint when oriented vertically. "Break" in the table indicates that the joint was broken during the particular cycle as indicated by the number in the same cell. "Intact" means that the joint remained intact after the number of cycles indicated in the same cell. "Intact*" means that the bonds did not break, but were

removed from the test during the cycle indicated by the number in the cell because three other bonds in the sequence had broken.

TABLE 4

Final rinse	Stress durability test						MCTF*
	1-top	2	3	4	5	6-bot	
Ca(HCO ₃) ₂	8 Intact*	8 Intact*	8 Break	8 Break	8 Intact*	6 Break	8
Ca(NO ₃) ₂	10 Intact*	10 Intact*	10 Intact*	10 Break	5 Break	9 Break	9
Ca(H ₂ PO ₄) ₂	41 Intact*	41 Intact*	41 Intact*	41 Break	25 Break	35 Break	37
Ca(NO ₂) ₂	45 Intact	45 Intact	45 Intact	45 Intact	20 Break	19 Break	37
DI	45 Intact	45 Intact	45 Intact	36 Break	45 Intact	25 Break	40
CaSO ₄	45 Intact	45 Intact	45 Intact	45 Intact	45 Intact	24 Break	42
Tap	45 Intact	45 Intact	45 Intact	45 Intact	45 Intact	25 Break	42

*MCTF = mean cycle to failure

5 The results above demonstrate that the final rinse can be critical to the bond durability. Table 4 shows that the final rinse performed with different calcium salts exhibits varying bond durability performance. The bonds rinsed with CaSO₄-enriched water and Georgia tap water provided the highest mean cycle to failure and only one broken bond. Ca(NO₂)₂ and DI water each resulted in two broken bonds. Ca(HCO₃)₂, Ca(NO₃)₂, and Ca(H₂PO₄)₂ each resulted in
10 three broken bonds and did not complete the nominal requirement of 45 cycles. The results show that tap water as the final rinse maintains or improves the pretreatment performance, as compared to DI water. In addition, the particular anions of the Ca²⁺ salts affect the bond durability performance.

15 Table 5 shows the stress durability performance of the pretreated AA6111 samples with a rinse using solutions of different Ca²⁺ salts, followed by an optional additional rinse step in DI water for 5 seconds. Each of the Ca²⁺ salt solutions had a Ca²⁺ concentration of 200 ppm. The results are shown in Table 5. In Table 5, each of the joints are numbered 1 through 6, where joint 1 is the top joint and joint 6 is the bottom joint when oriented vertically. "Break" in the

table indicates that the joint was broken during the particular cycle as indicated by the number in the same cell. "Intact" means that the joint remained intact after the number of cycles indicated in the same cell. "Intact*" means that the bonds did not break, but were removed from the test during the cycle indicated by the number in the cell because three other bonds in the sequence had broken.

TABLE 5

Final rinse	Extra rinse	Ti weight (mg/m ²)	Stress durability test						MCTF*
			1-top	2	3	4	5	6-bot	
Ca(HCO ₃) ₂	n/a	21.3	8 Intact*	8 Intact*	8 Break	8 Break	8 Intact*	6 Break	8
Ca(NO ₃) ₂	n/a	11.3	10 Intact*	10 Intact*	10 Intact*	10 Break	5 Break	9 Break	9
Ca(H ₂ PO ₄) ₂	n/a	16.2	41 Intact*	41 Intact*	41 Intact*	41 Break	25 Break	35 Break	37
Ca(HCO ₃) ₂	DI	12.8	45 Intact	40 Break	45 Intact	45 Intact	35 Break	45 Intact	43
CaSO ₄	n/a	17.6	45 Intact	45 Intact	45 Intact	45 Intact	45 Intact	24 Break	42
Ca(H ₂ PO ₄) ₂	DI	14.9	45 Intact	45 Intact	45 Intact	45 Intact	45 Intact	30 Break	43
Ca(NO ₃) ₂	DI	15.9	45 Intact	45 Intact	45 Intact	45 Intact	34 Break	45 Intact	43
CaSO ₄	DI	15.5	45 Intact	45 Intact	45 Intact	45 Intact	45 Intact	45 Intact	45

*MCTF = mean cycle to failure

As shown in Table 5, the bonds lasted for more cycles and the performance was significantly improved for the samples rinsed with Ca²⁺ solutions and additionally rinsed with DI water. This is attributed to the existence of pretreatment residues that were not tightly adhered to the substrate, as shown by the Ti coat weight drop by approximately 2 mg/m² after the extra DI water rinse.

All patents, patent applications, publications, and abstracts cited above are incorporated herein by reference in their entirety. Various embodiments of the invention have been described in fulfillment of the various objectives of the invention. It should be recognized that these

embodiments are merely illustrative of the principles of the present invention. Numerous modifications and adaptations thereof will be readily apparent to those of skill in the art without departing from the spirit and scope of the invention as defined in the following claims.

WHAT IS CLAIMED IS:

1. A method for treating a metal surface, comprising:
contacting a metal surface one or more times with an aqueous agent comprising at least about 7 ppm calcium ions, wherein the metal surface is coated with a pretreatment coating comprising fluoride ions.
2. A method for pretreating a metal surface, comprising:
coating a metal surface with a pretreatment coating; and
contacting the metal surface coated with the pretreatment coating with an aqueous agent comprising at least 7 ppm calcium ions.
3. A method of improving corrosion resistance of a metal surface, comprising:
coating a metal surface with a pretreatment coating; and
contacting the metal surface coated with the pretreatment coating with an aqueous agent comprising at least 7 ppm calcium ions.
4. The method of any of claims 1-3, wherein the metal surface comprises an aluminum alloy surface.
5. The method of claim 4, wherein the aluminum alloy surface comprises a surface of a 2xxx, 3xxx, 5xxx, 6xxx or 7xxx aluminum alloy.
6. The method of any of claims 1-5, wherein the pretreatment coating comprises a Ti/Zr or Zr/Cr coating.
7. The method of any of claims 1-5, wherein the pretreatment coating comprises a hexafluorotitanate, hexafluorozirconate or chromium sulfate coating.

8. The method of any of claims 1-7, further comprising, after the contacting step, applying to the metal surface one or more of a paint, a lacquer, an adhesive, a glue or a bonding compound.
9. The method of any of claims 1-8, wherein the aqueous agent comprises a solution of a calcium salt.
10. The method of claim 9, wherein the calcium salt comprises a calcium carbonate, a calcium phosphate, a calcium nitrate or a calcium sulfate.
11. The method of any of claims 1-8, wherein the aqueous agent comprises a solution of calcium carbonate.
12. The method of claim 11, wherein the aqueous agent comprises a saturated solution of calcium carbonate.
13. The method of any of claims 1-12, wherein the aqueous agent comprises calcium ions in an amount of at least about 7.5 ppm.
14. The method of any of claims 1-13, wherein the aqueous agent comprises about 7.5 ppm to 9.8 ppm of calcium ions.
15. The method of any of claims 1-14, wherein the aqueous agent comprises calcium ions at saturation.
16. The method of any of claims 1-15, wherein the step of contacting the metal surface with the aqueous agent comprises one or more of immersing the metal surface in the agent, rinsing the metal surface with the agent, rolling the agent onto the metal surface, or spraying the metal surface with the agent.

17. The method of any of claims 1-16, wherein fluoride ion content is reduced in the pretreatment coating after the contacting step or wherein the calcium ion content is increased in the pretreatment coating after the contacting step.

18. The method of any of claims 1-17, wherein the metal surface is rinsed with the aqueous agent in the contacting step, and the weight of the pretreatment coating after the contacting step is greater in comparison to a metal surface coated with the pretreatment coating rinsed with deionized water.

19. An article of manufacture comprising a metal surface treated by the method of any of claims 1-18.

20. The article of manufacture of claim 19, wherein the article is an aluminum alloy sheet, a motor vehicle panel, an automotive panel, an electronics panel, an architectural panel or a material comprising an aluminum alloy surface.

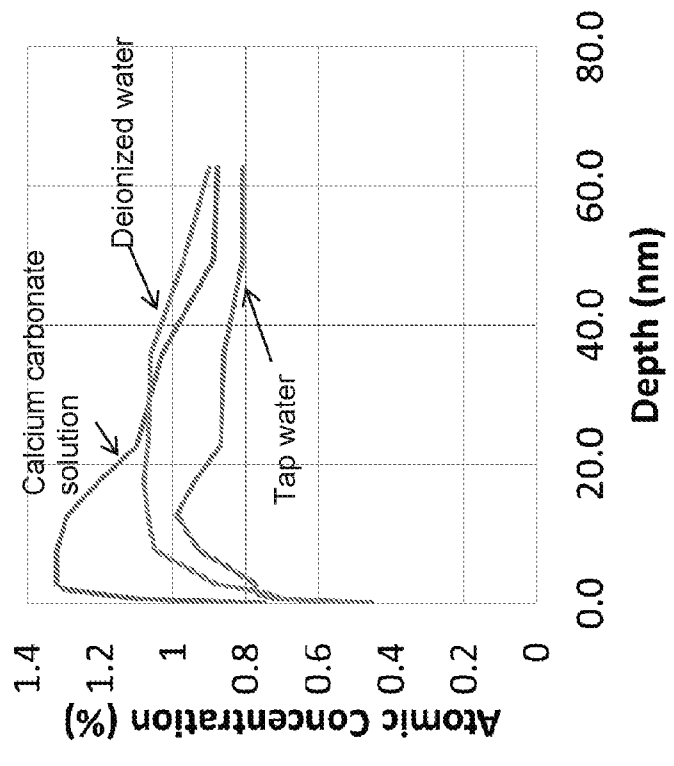


FIGURE 1A

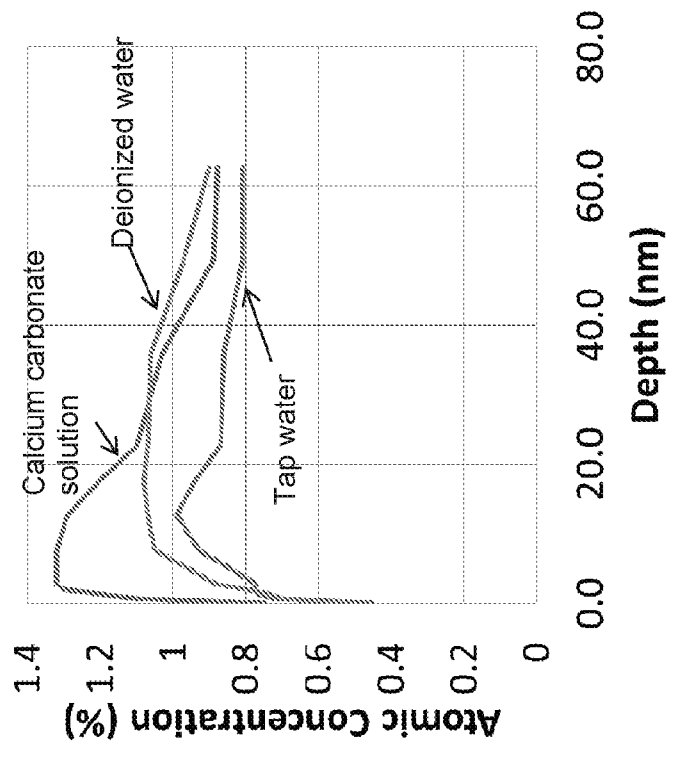


FIGURE 1B

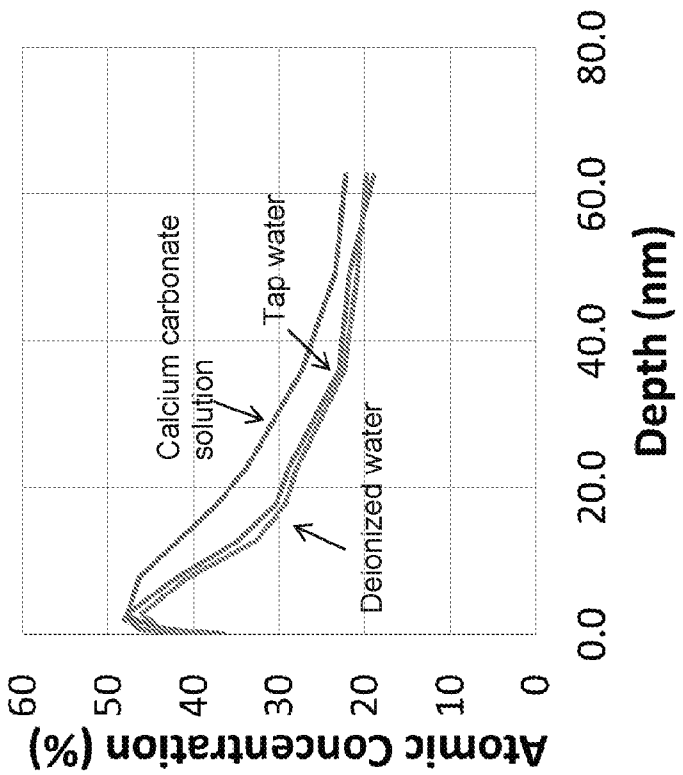


FIGURE 2B

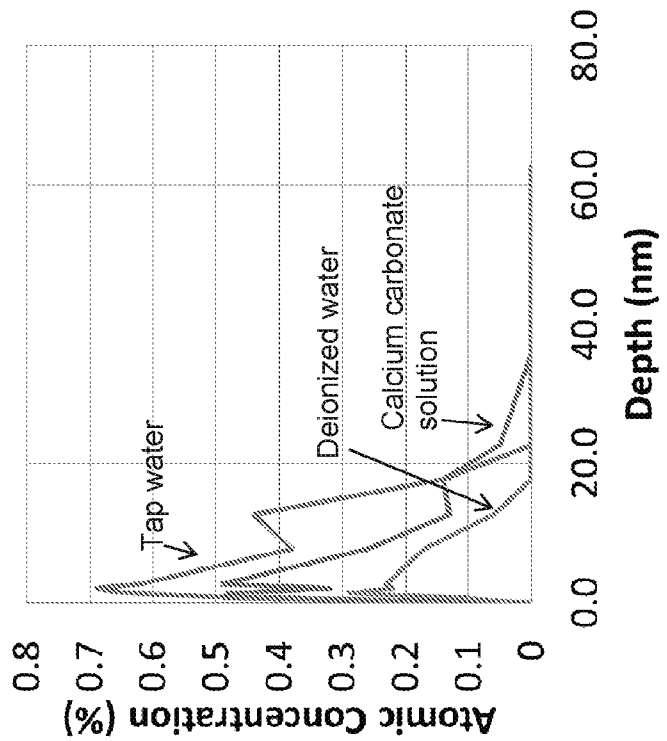


FIGURE 2A

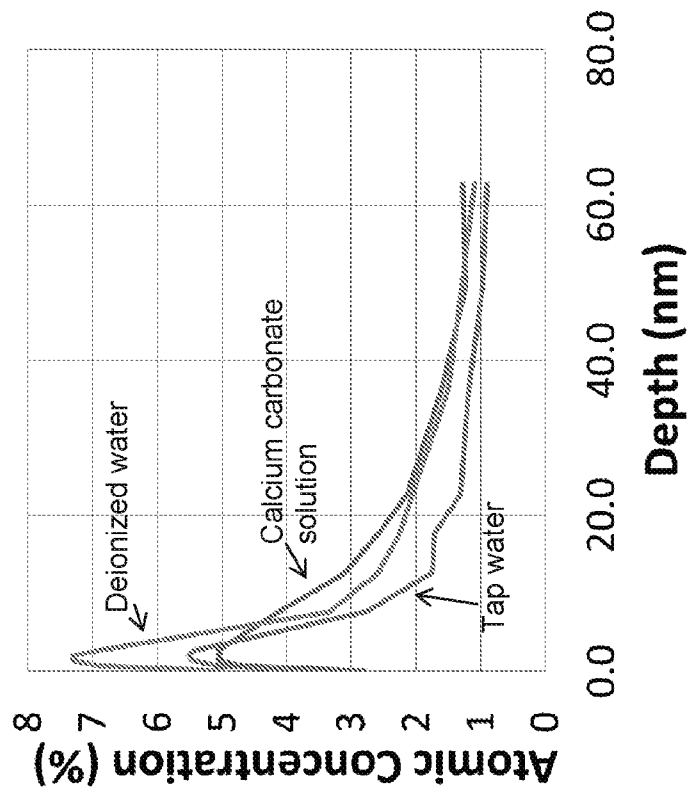


FIGURE 3A

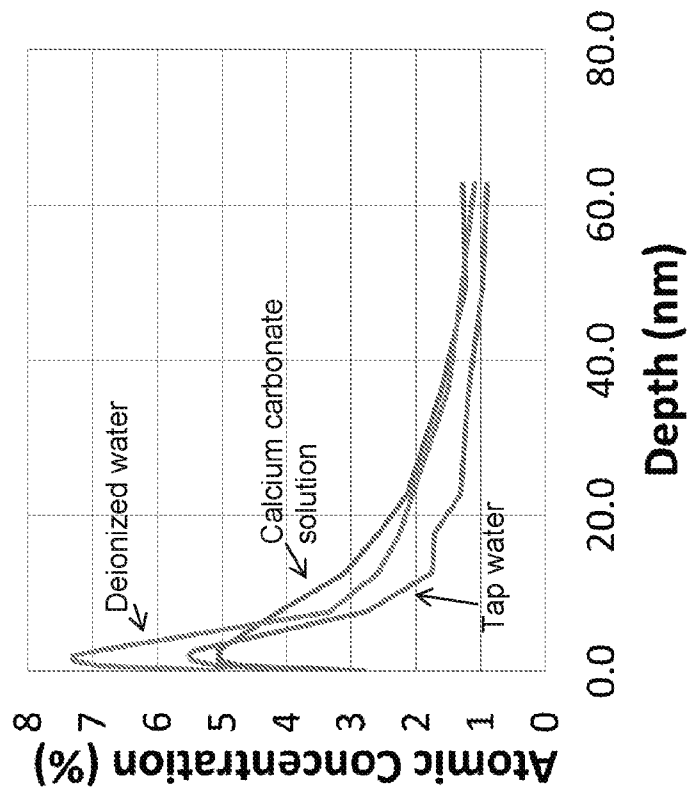


FIGURE 3B

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2015/064449

A. CLASSIFICATION OF SUBJECT MATTER

INV. C23C22/34 C23C22/83 C23C22/44
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

10 March 2016

Date of mailing of the international search report

08/04/2016

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2015/064449

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International application No

PCT/US2015/064449

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