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(54) **SYSTEMS AND METHODS FOR TREATING A SUBSTRATE**

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(57) **ABSTRACT**

Disclosed herein is a system for treating a magnesium or a magnesium alloy substrate comprising: a first pretreatment composition comprising a fluorometallic acid and free fluoride in an amount of 10 ppm to 500 ppm based on total weight of the first pretreatment composition and having a pH of 1.0 to 4.0; and a second pretreatment composition comprising a lanthanide series metal, the second pretreatment composition being substantially free of peroxide. Also disclosed are methods of treating a magnesium or magnesium alloy substrate. Treated magnesium and magnesium alloy substrates also are disclosed.

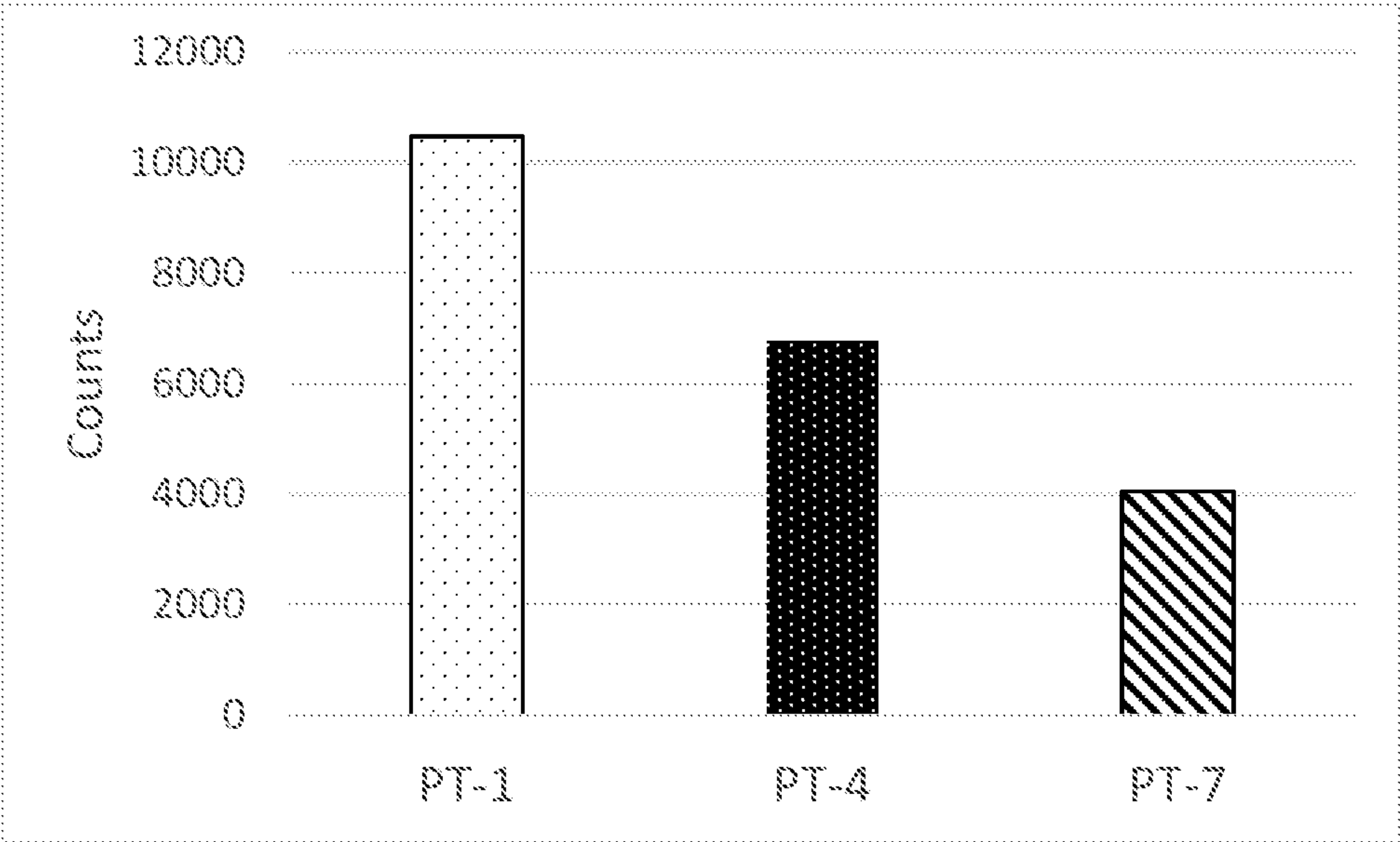


FIG. 1A

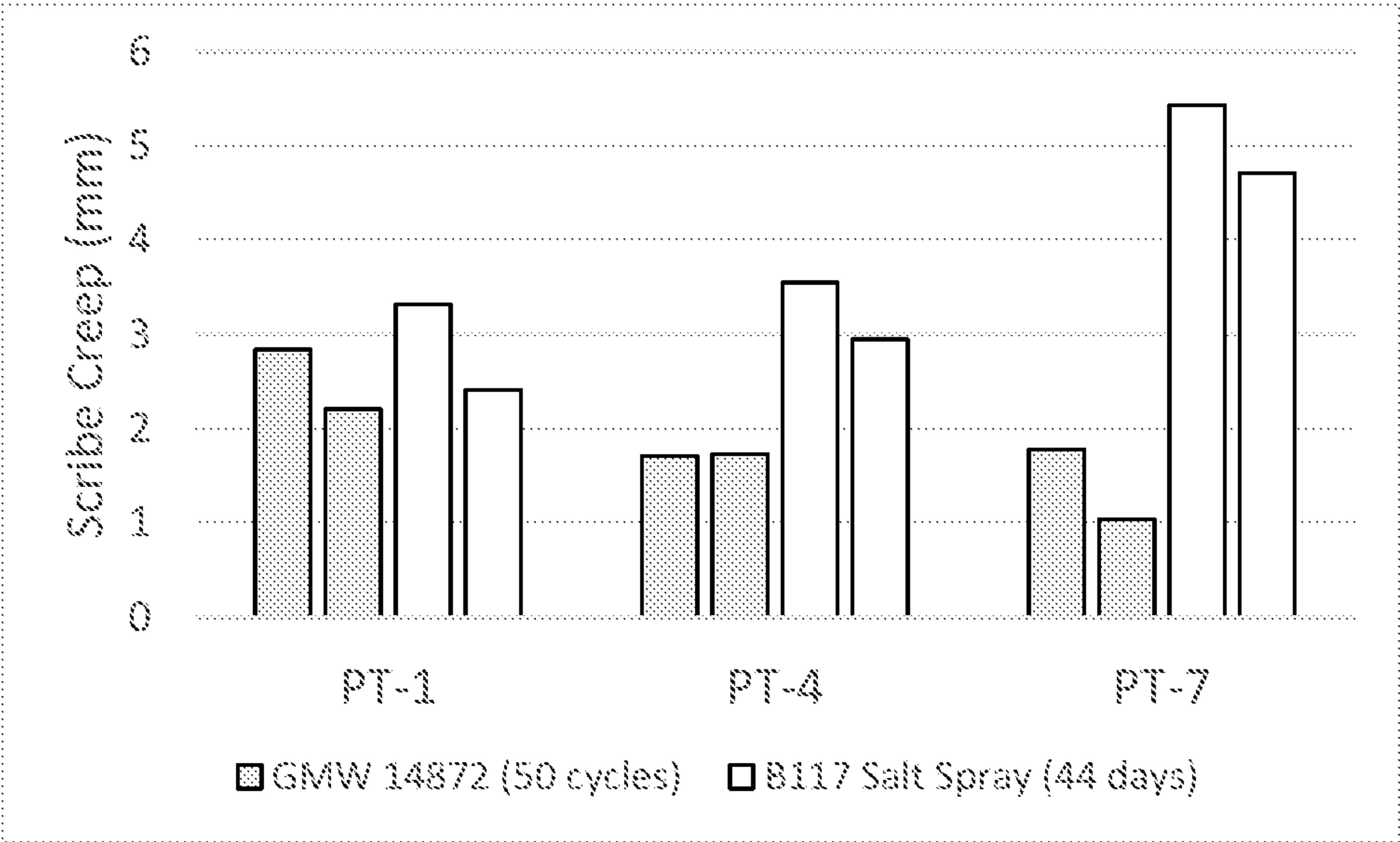


FIG. 1B

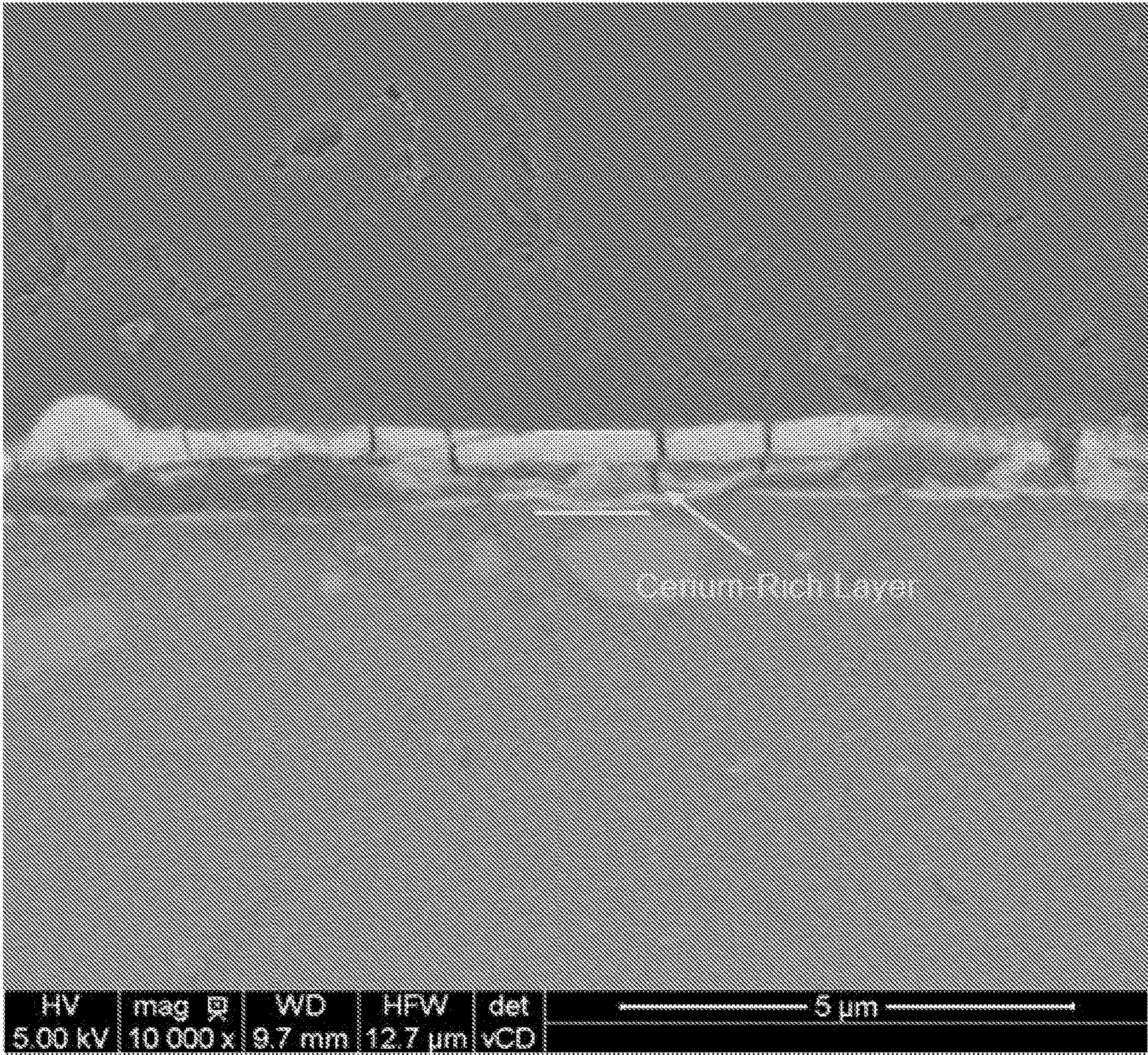


FIG. 1C

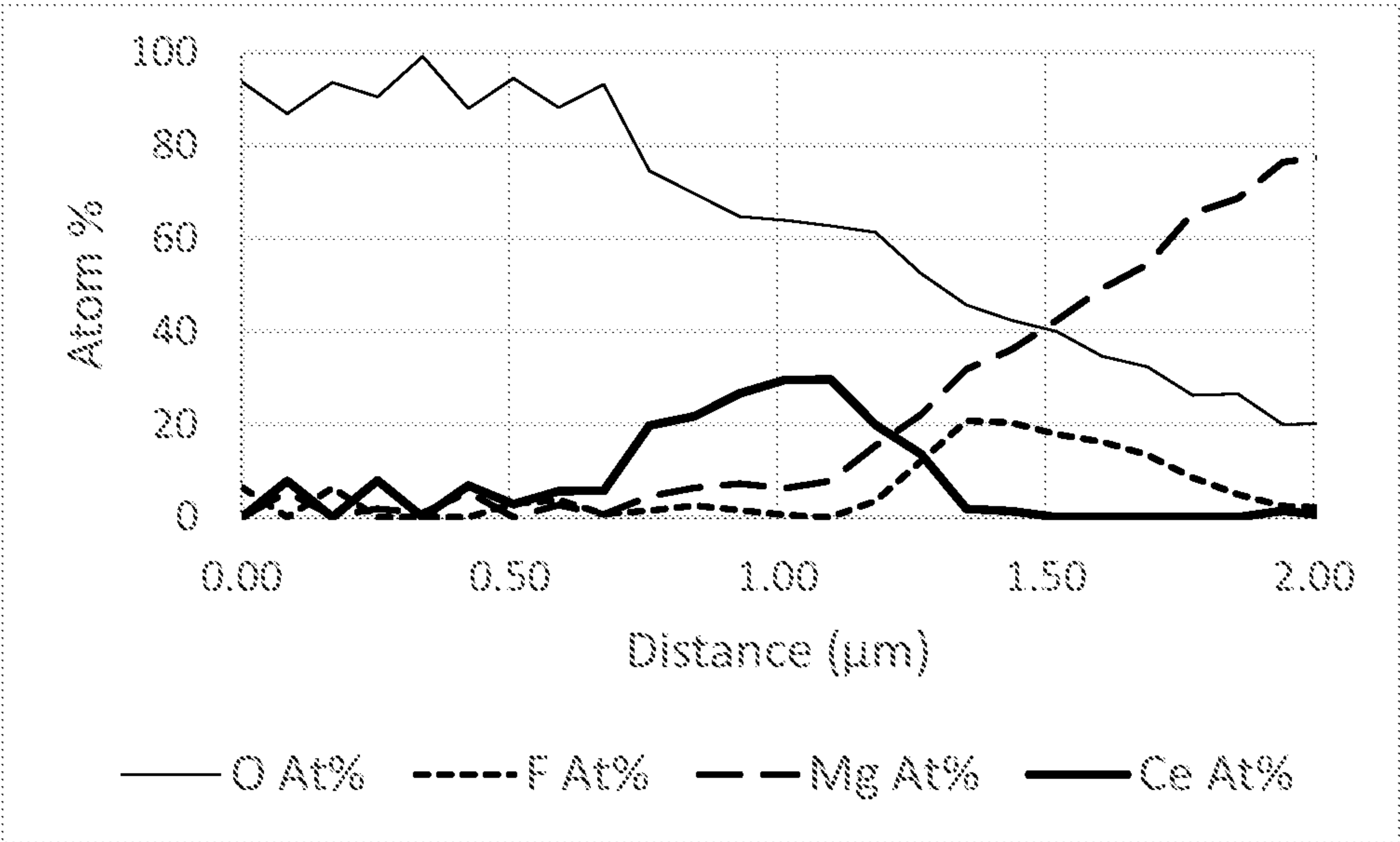


FIG. 1D

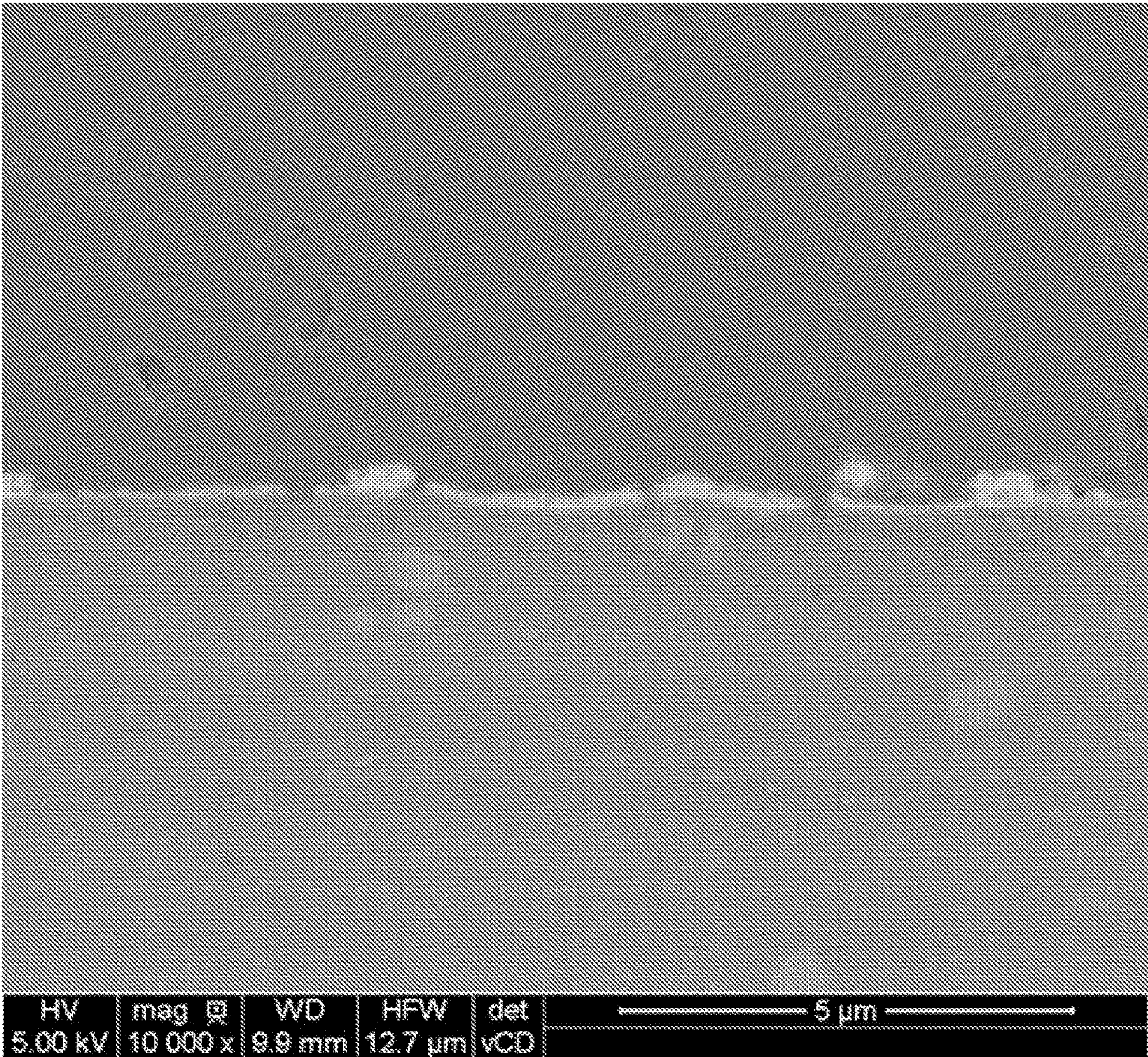


FIG. 1E

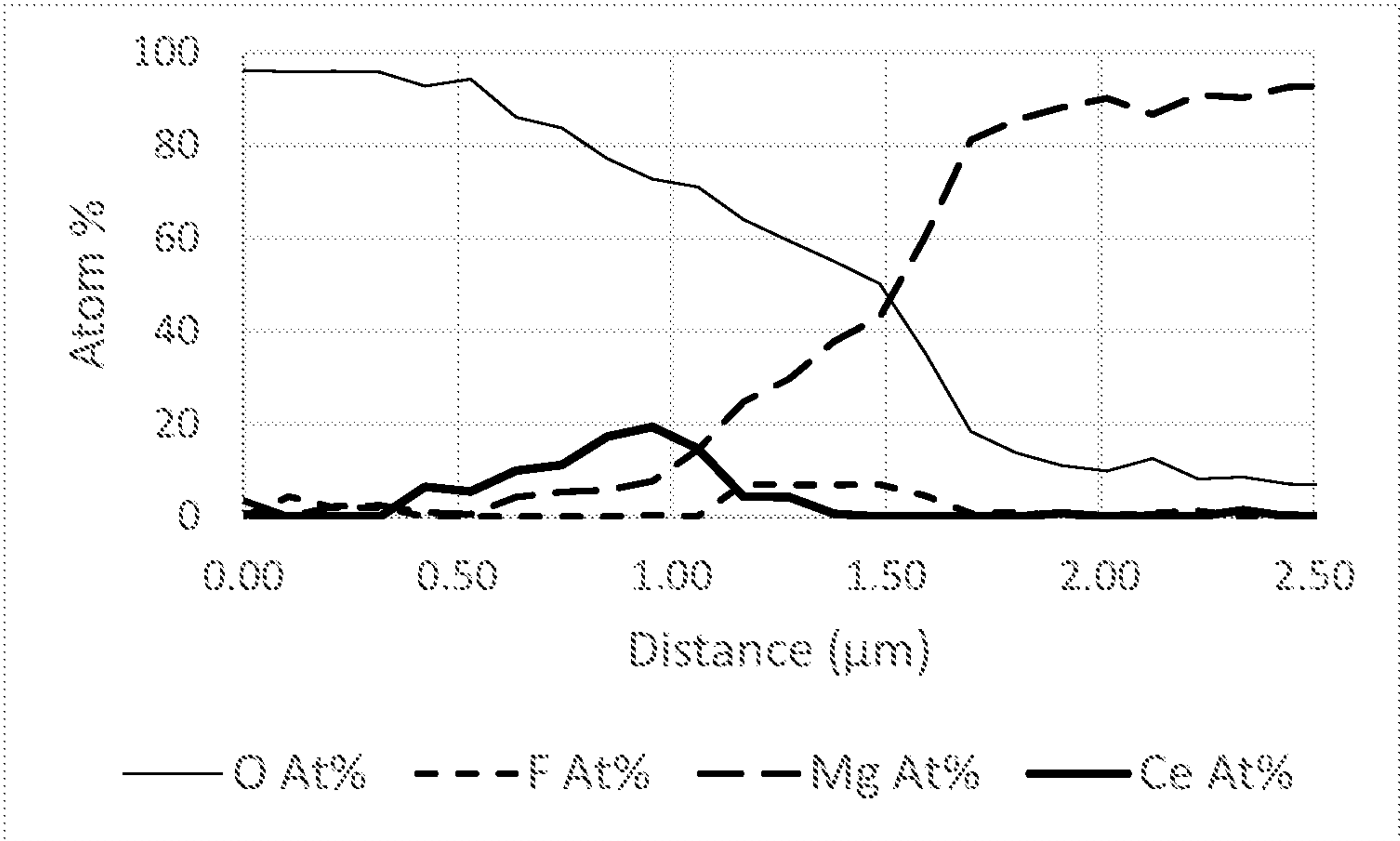


FIG. 1F

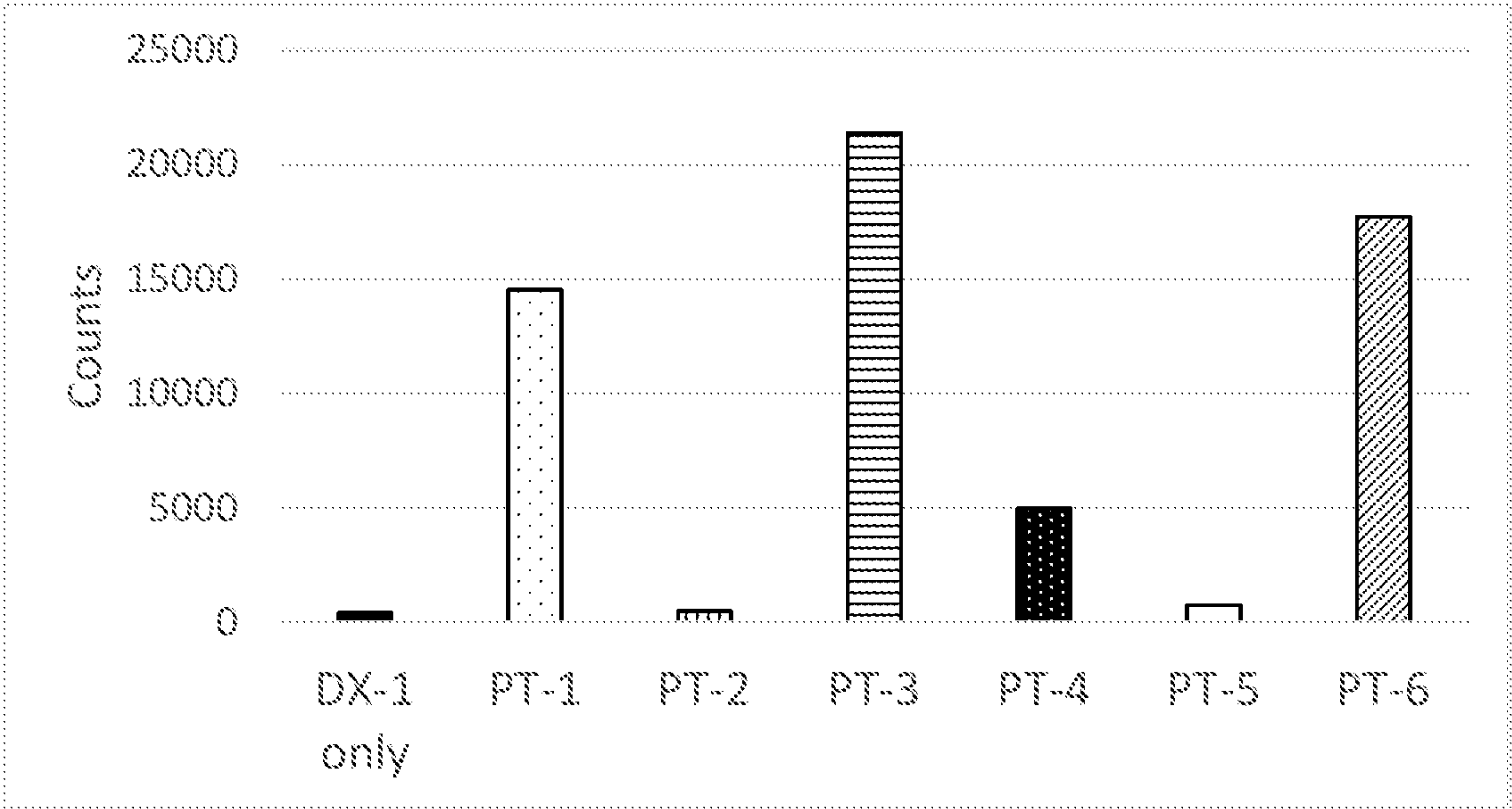


FIG. 2A

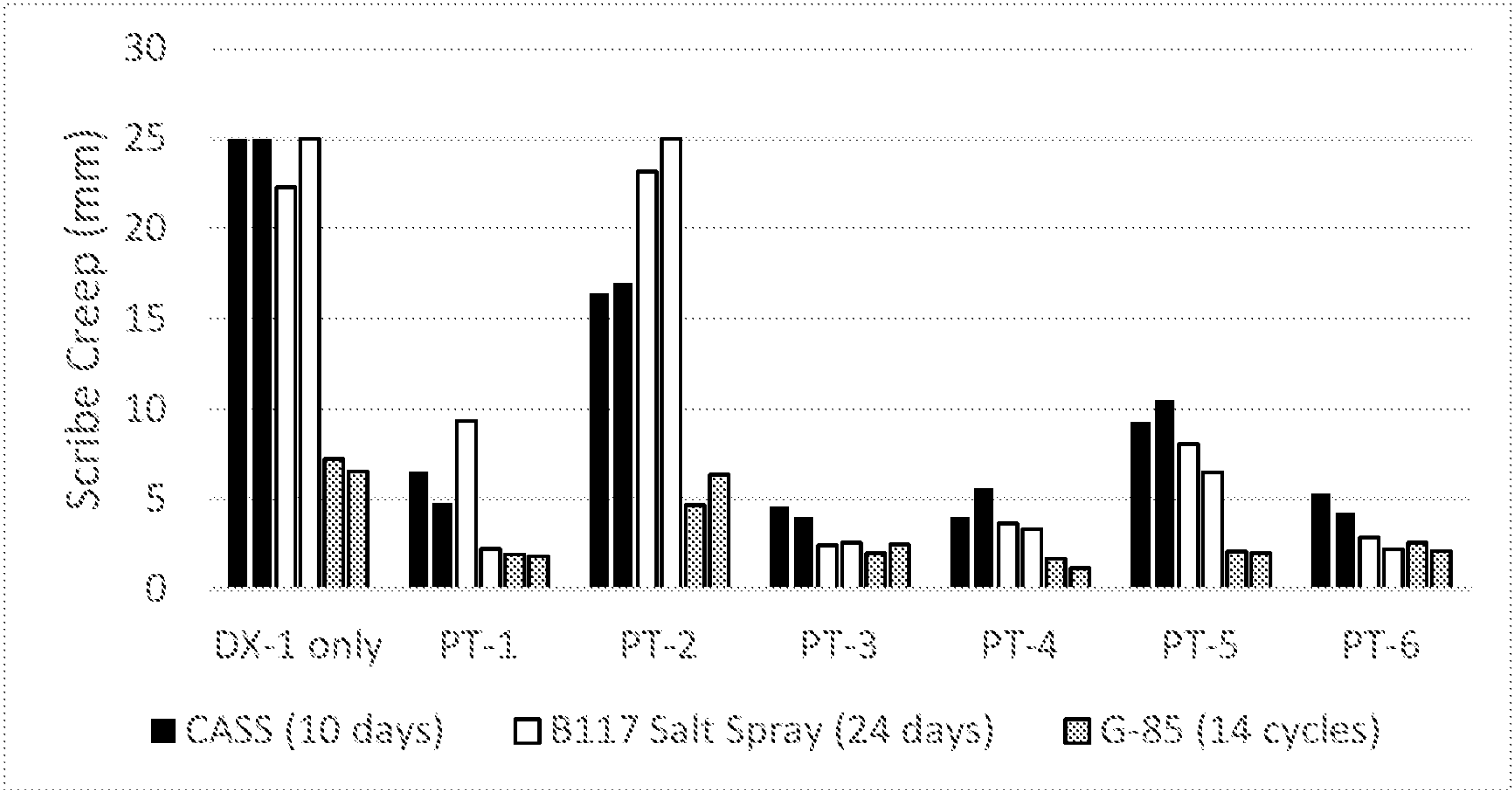


FIG. 2B

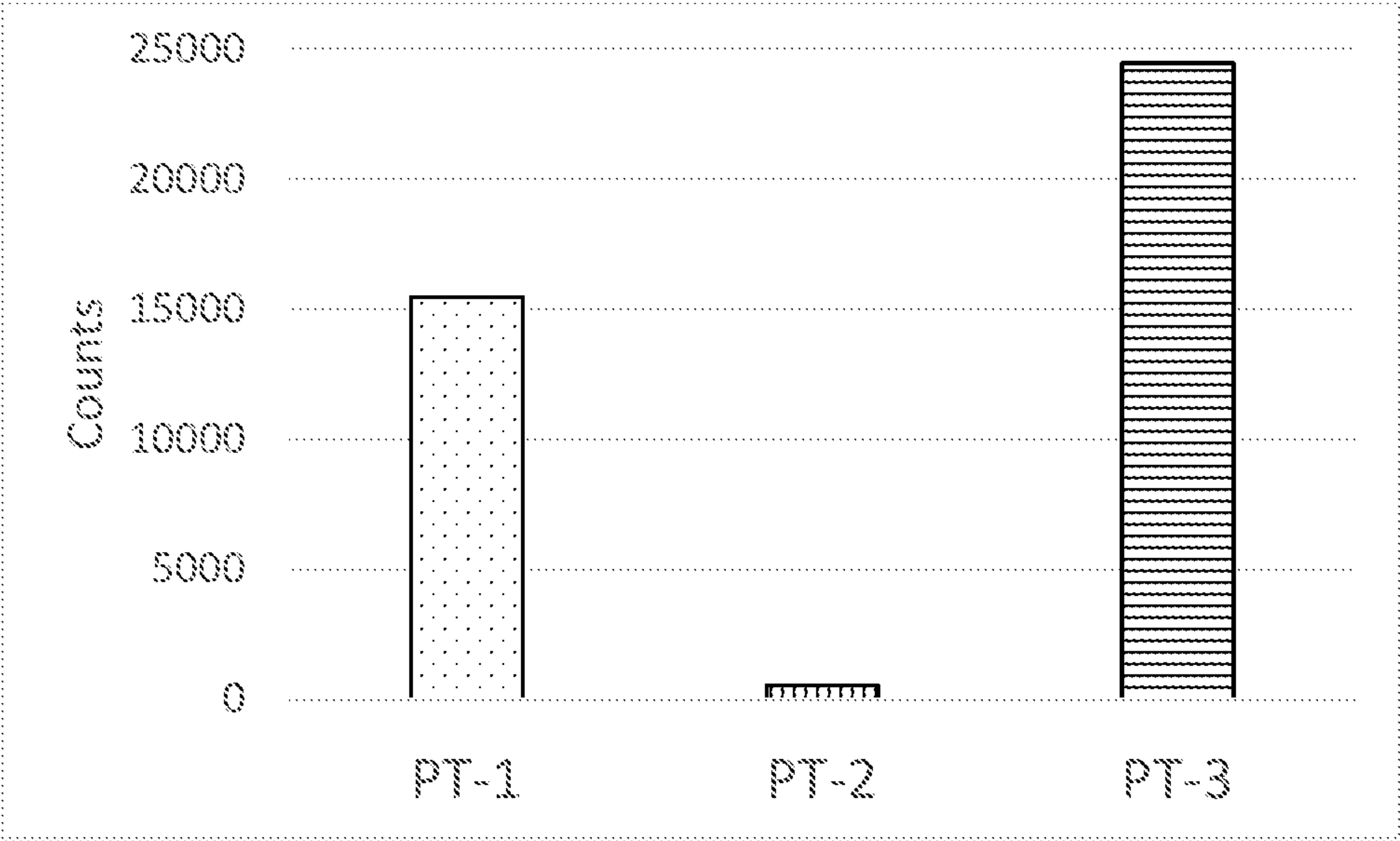


FIG. 3A

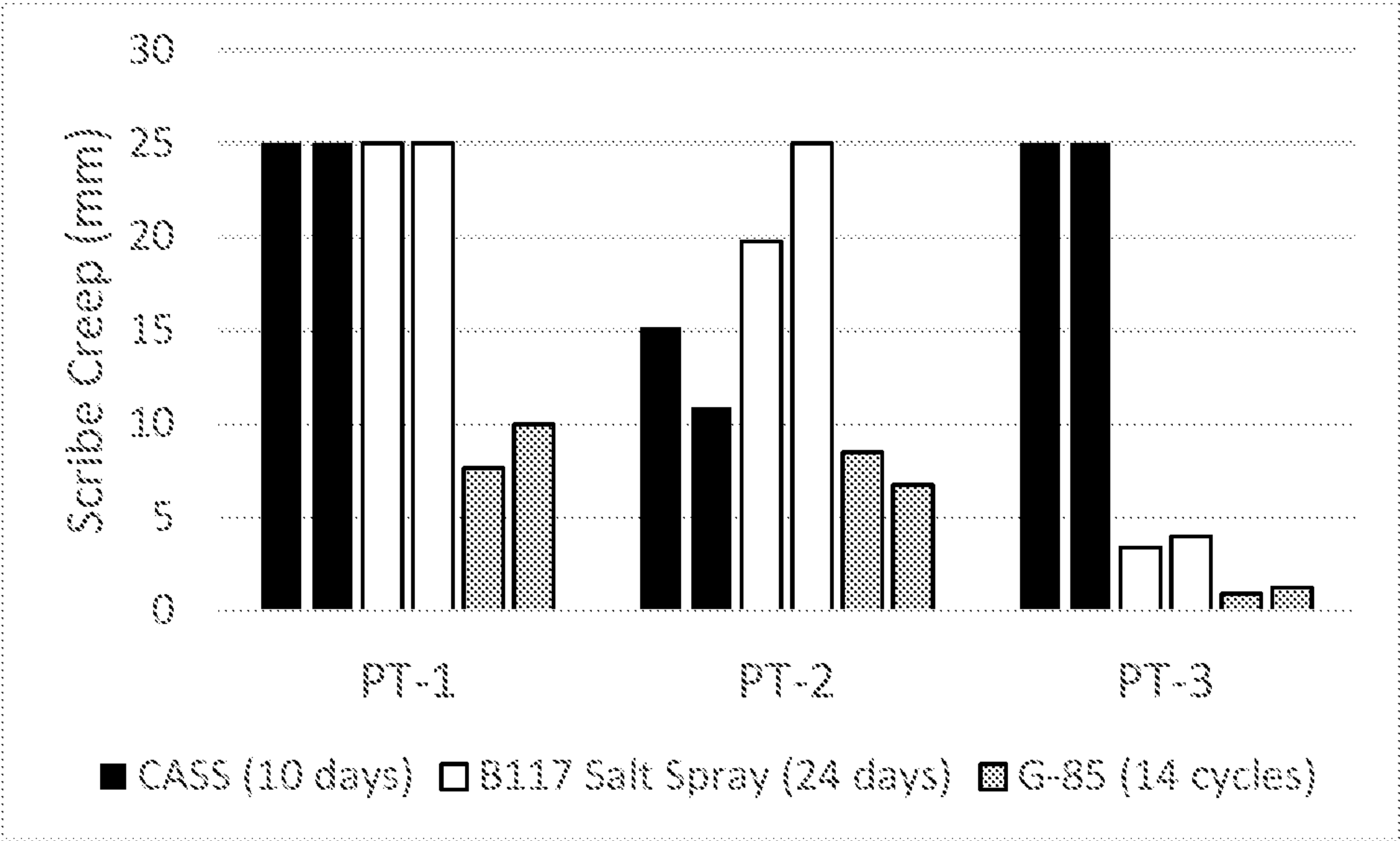


FIG. 3B

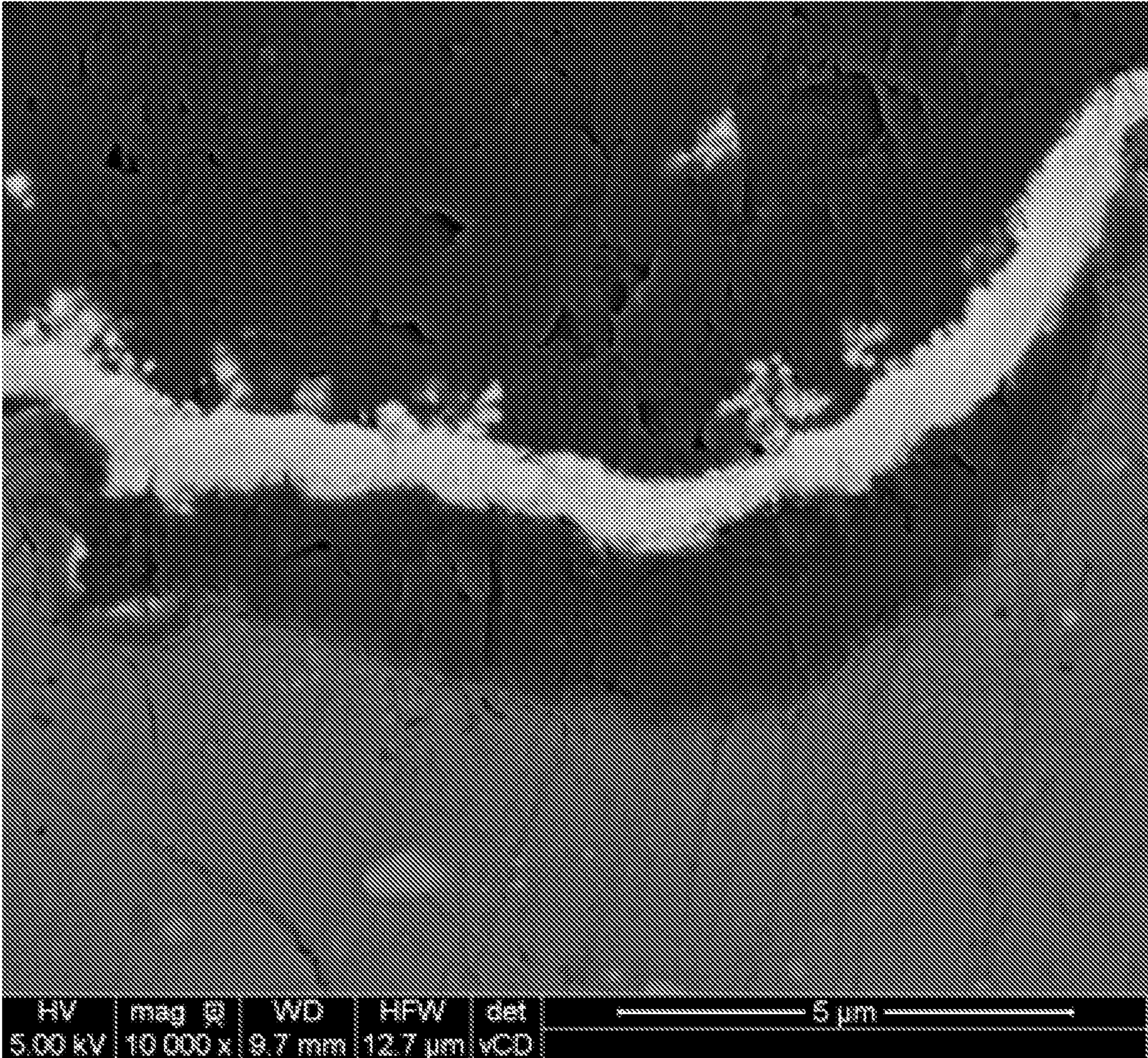


FIG. 3C

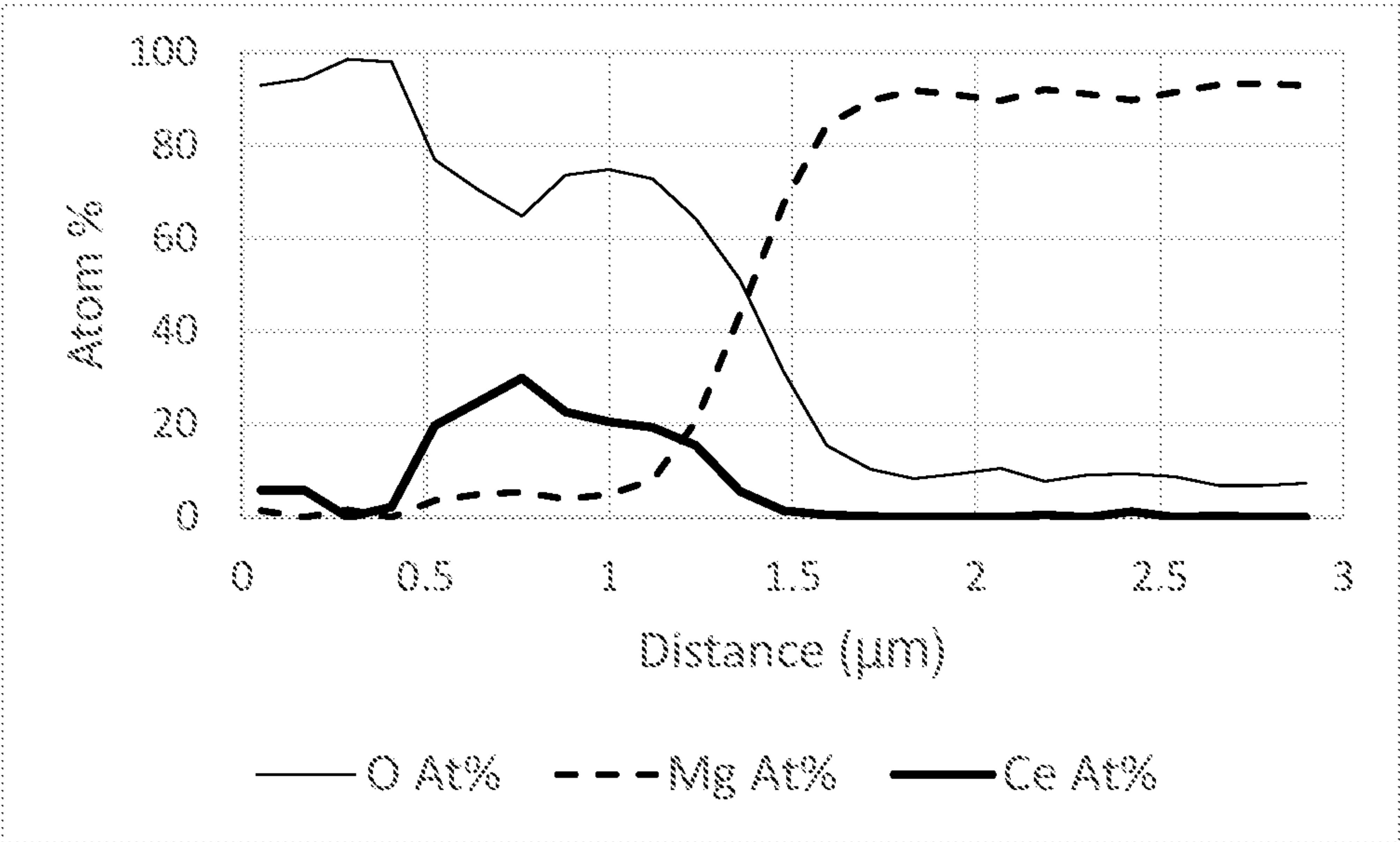


FIG. 3D

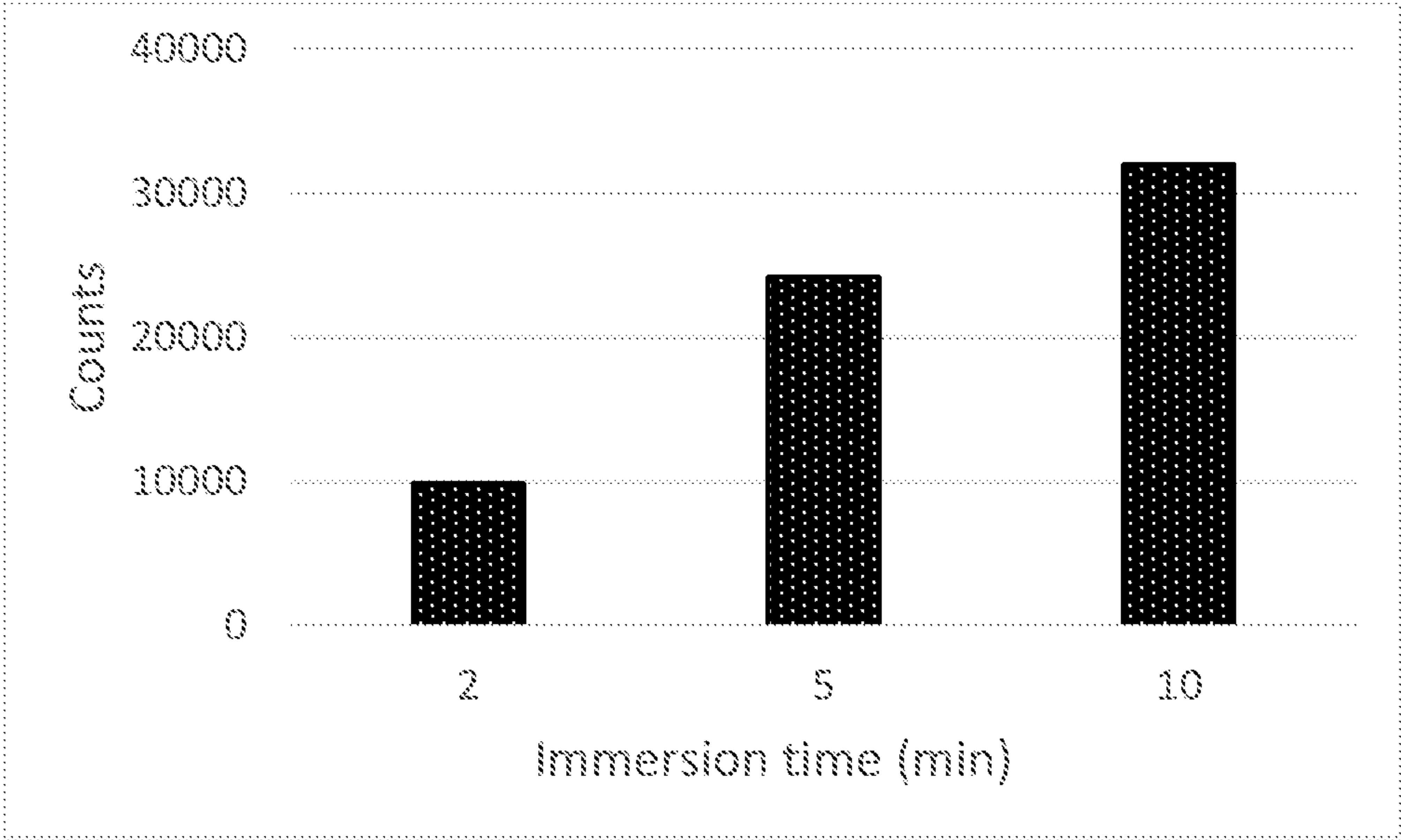


FIG. 4A

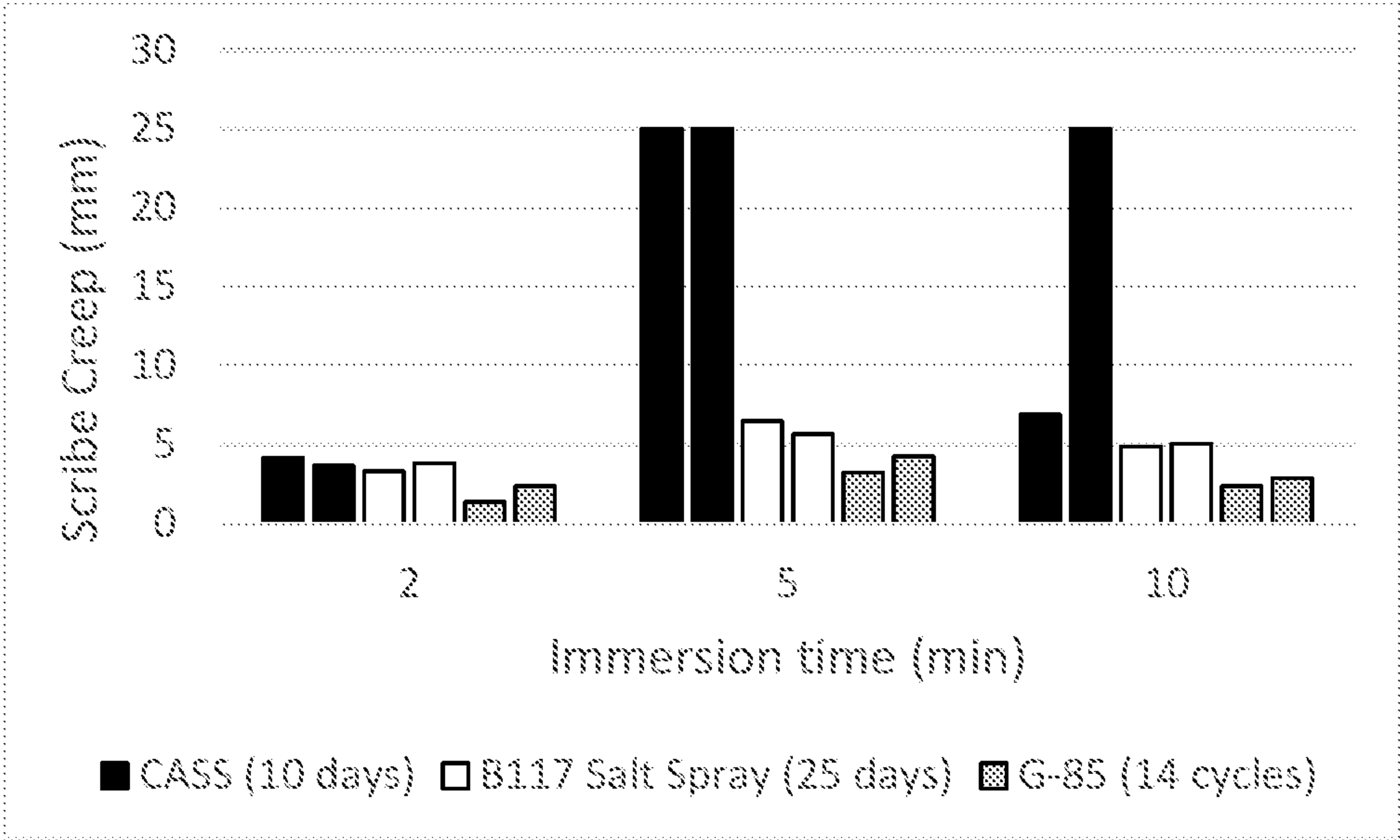


FIG. 4B

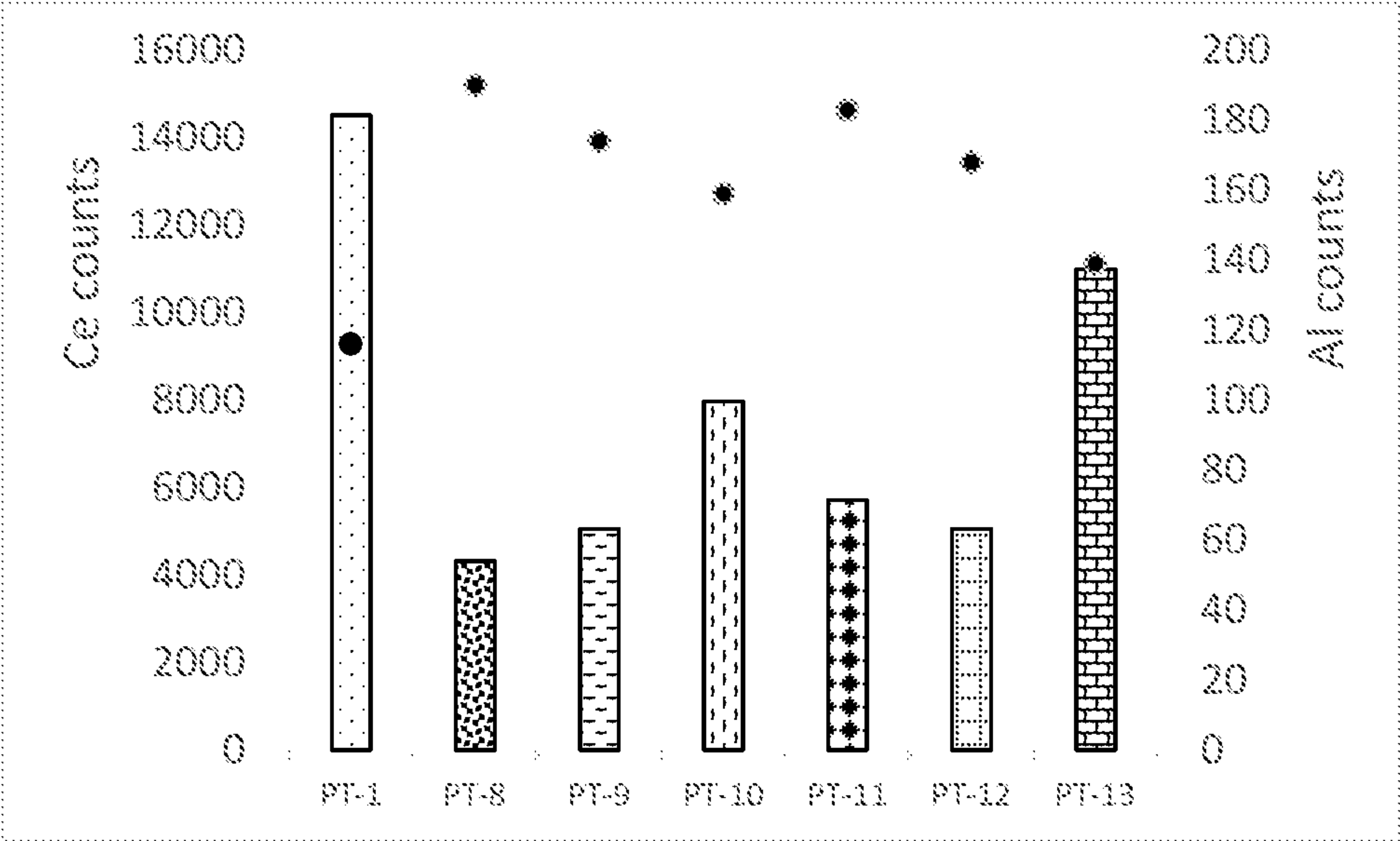


FIG. 5A

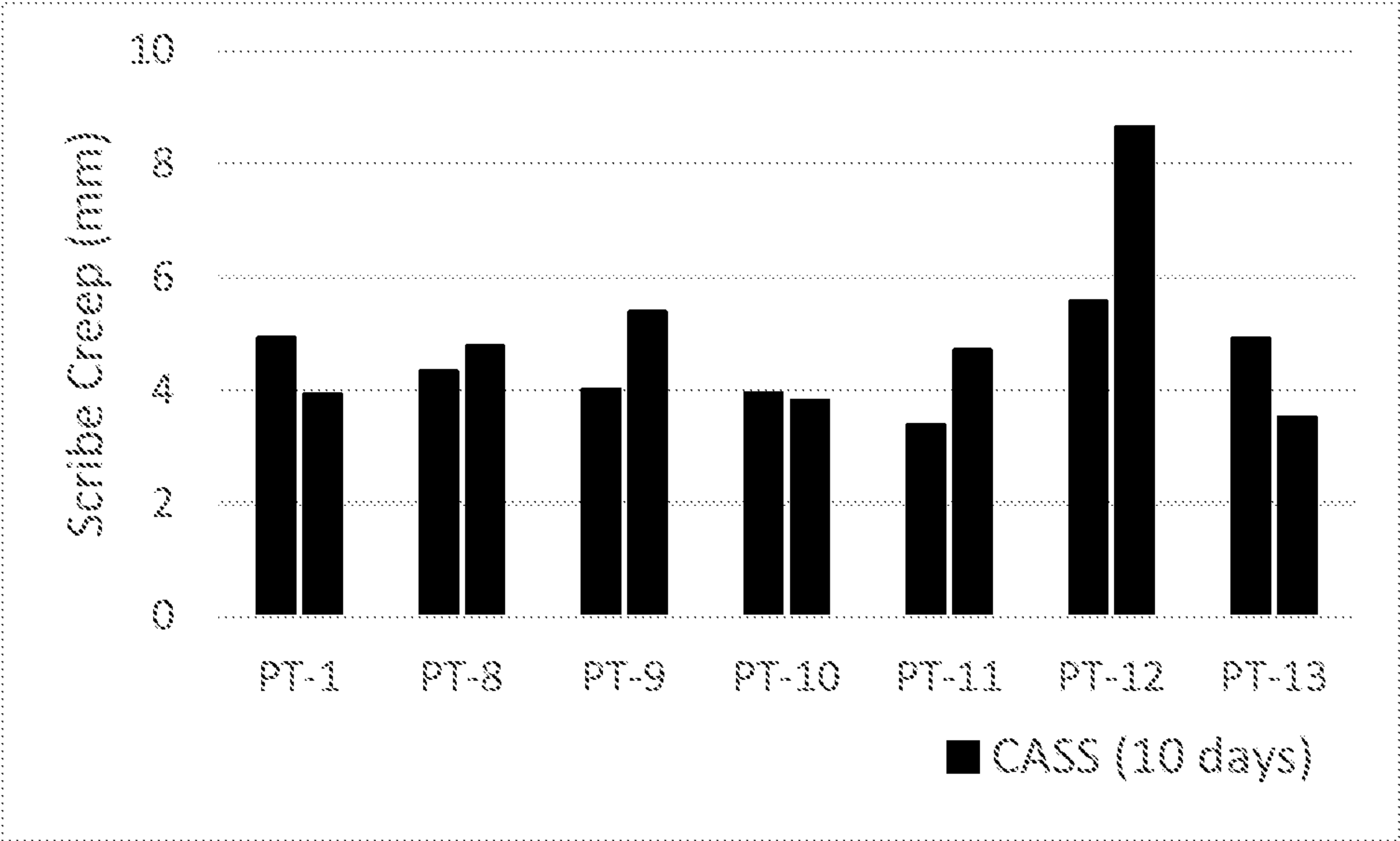


FIG. 5B

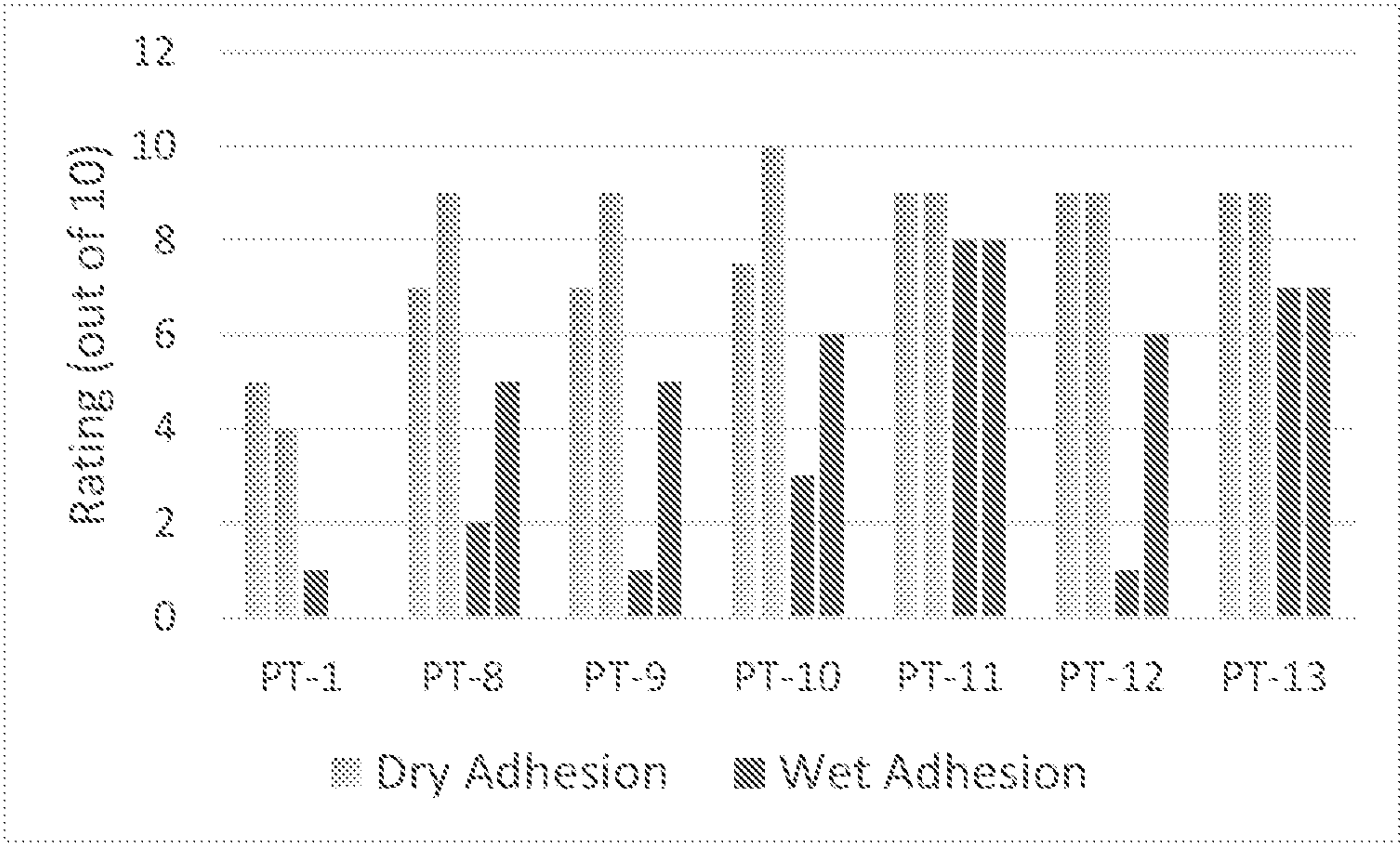


FIG. 5C

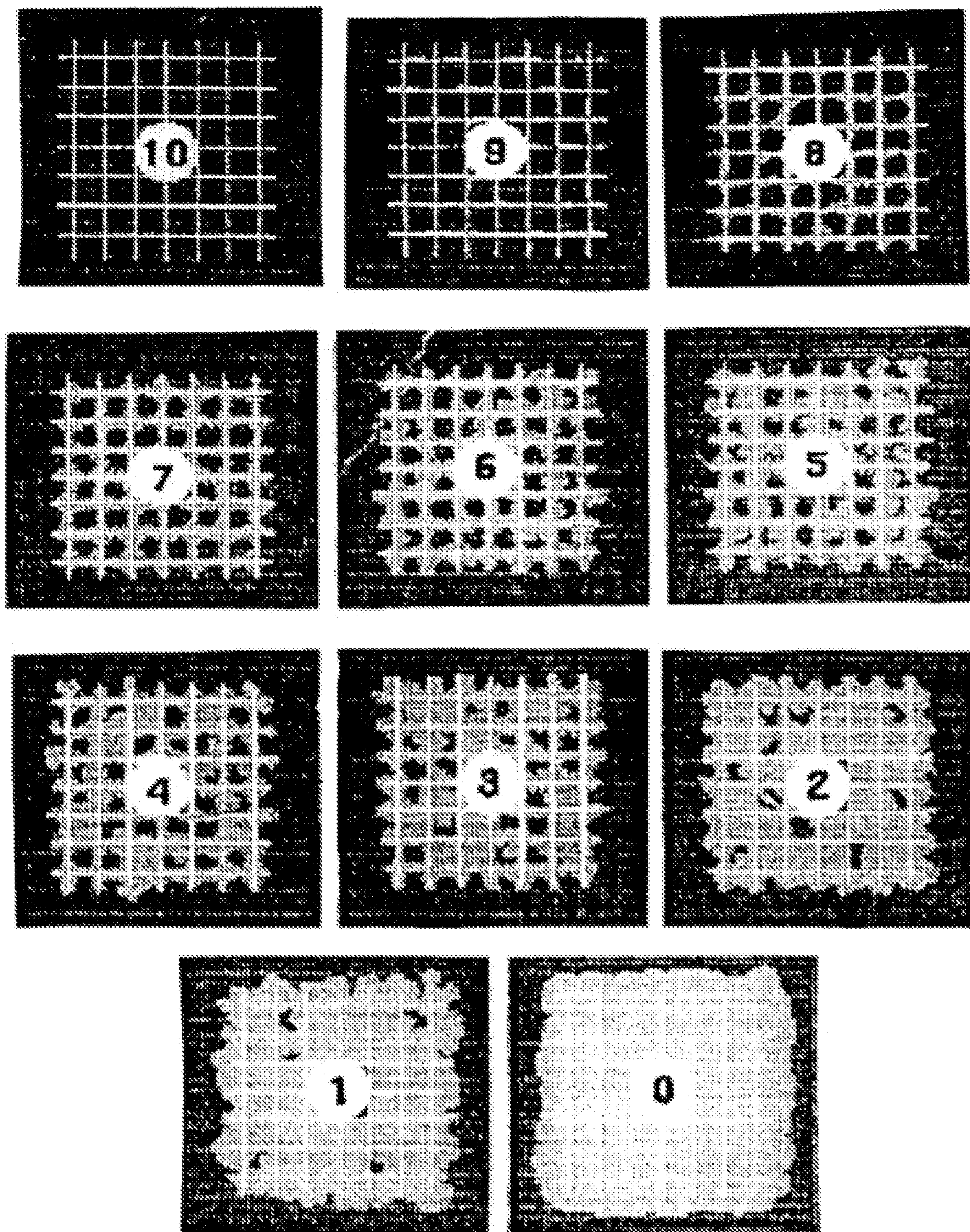


FIG. 5D

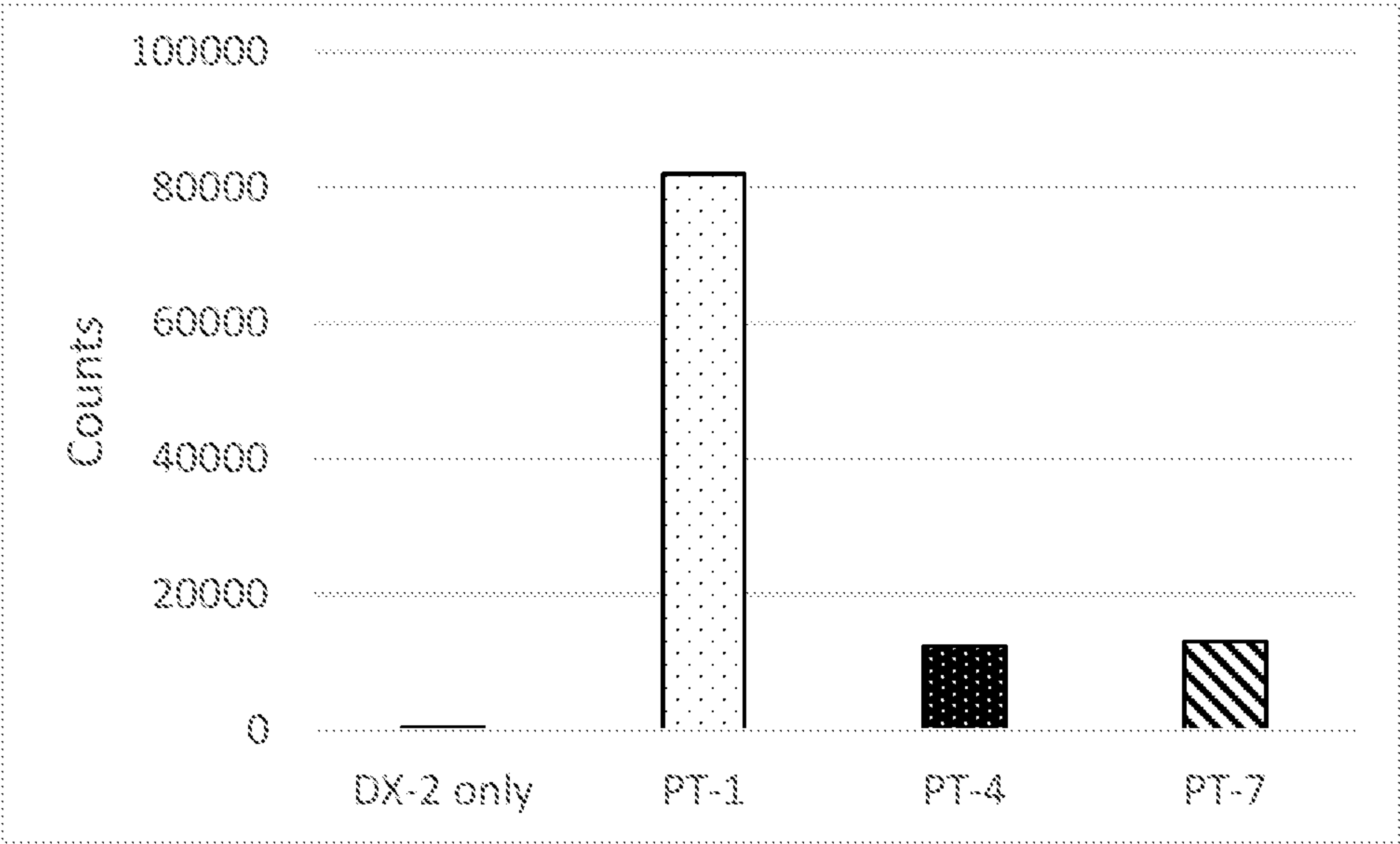


FIG. 6A

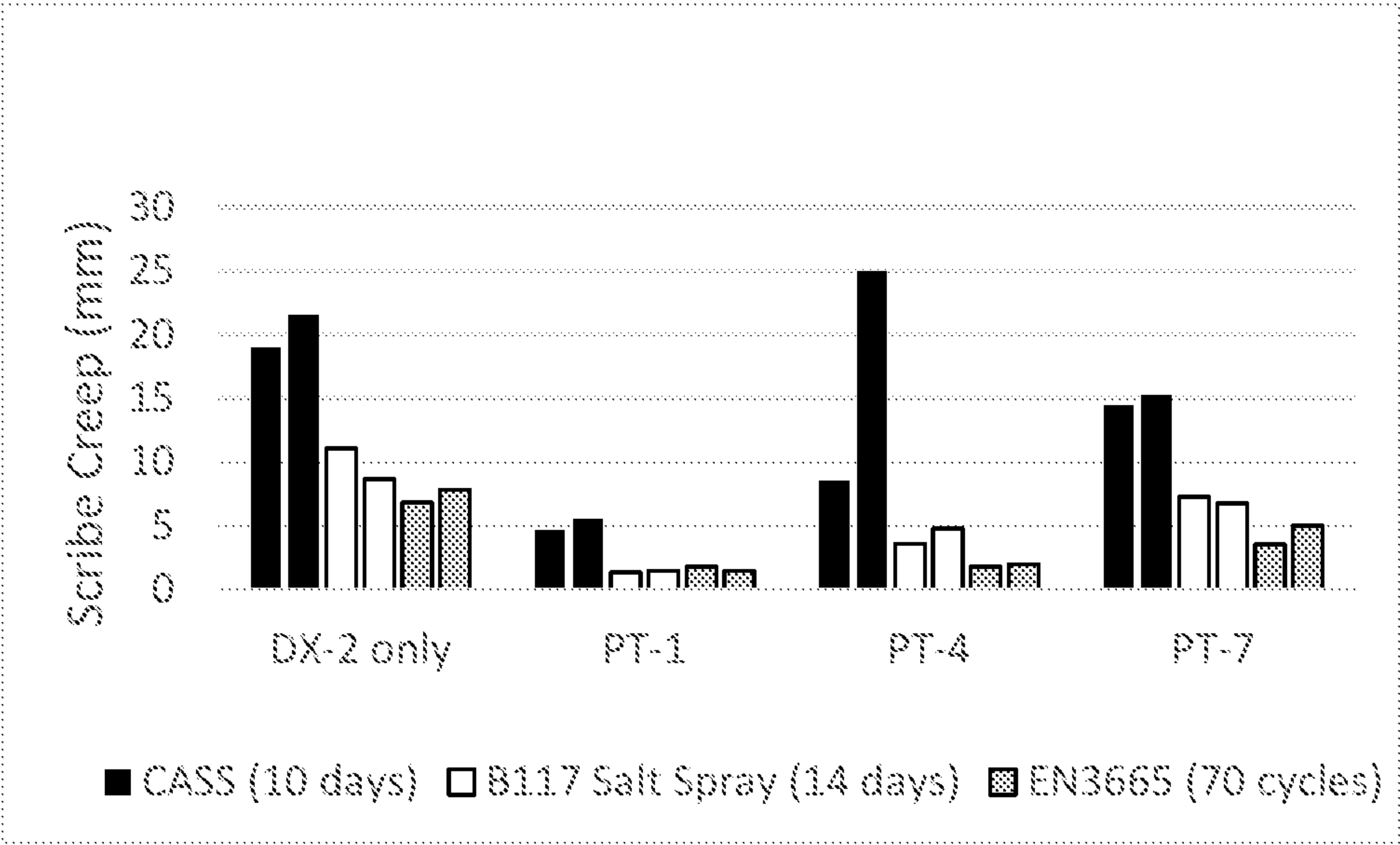


FIG. 6B

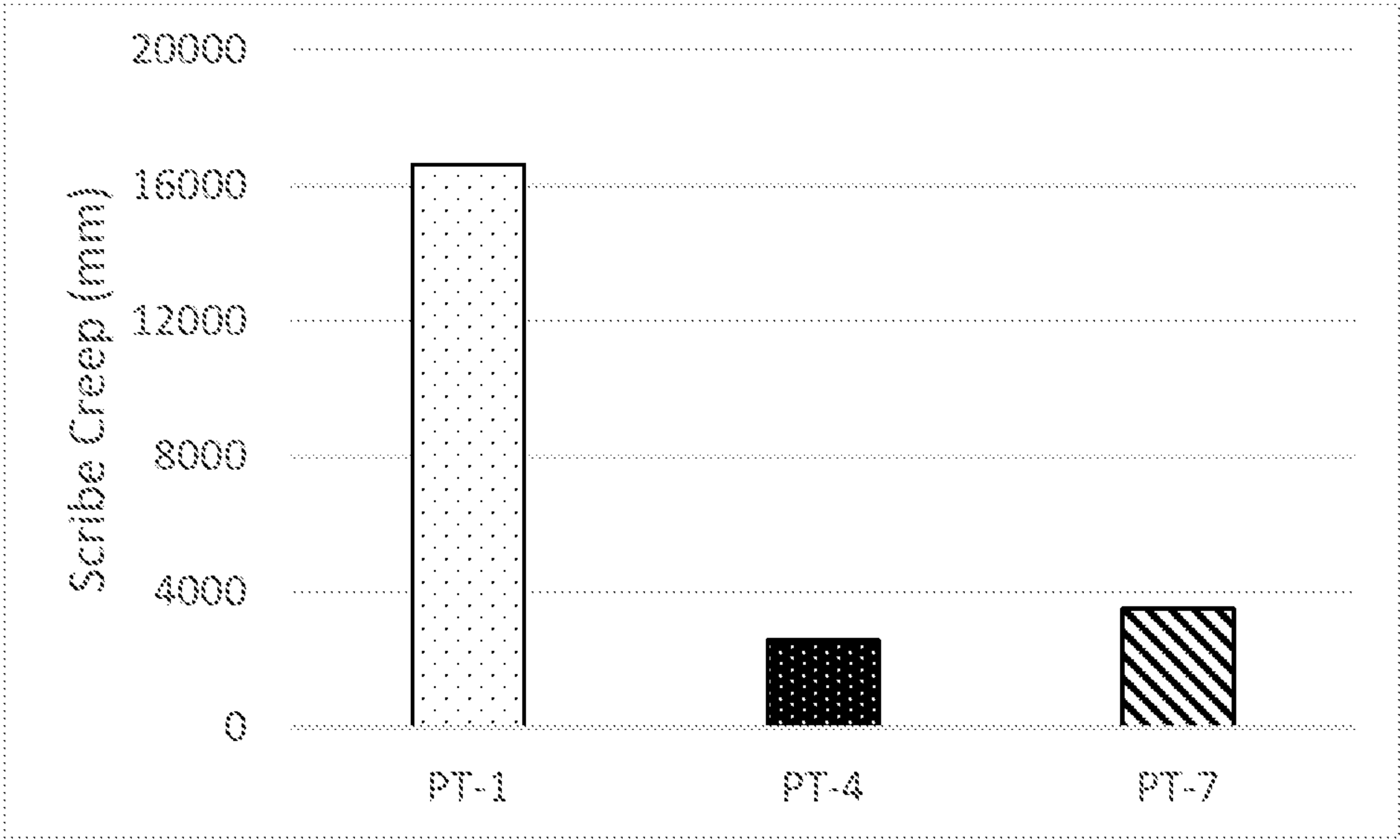


FIG. 7A

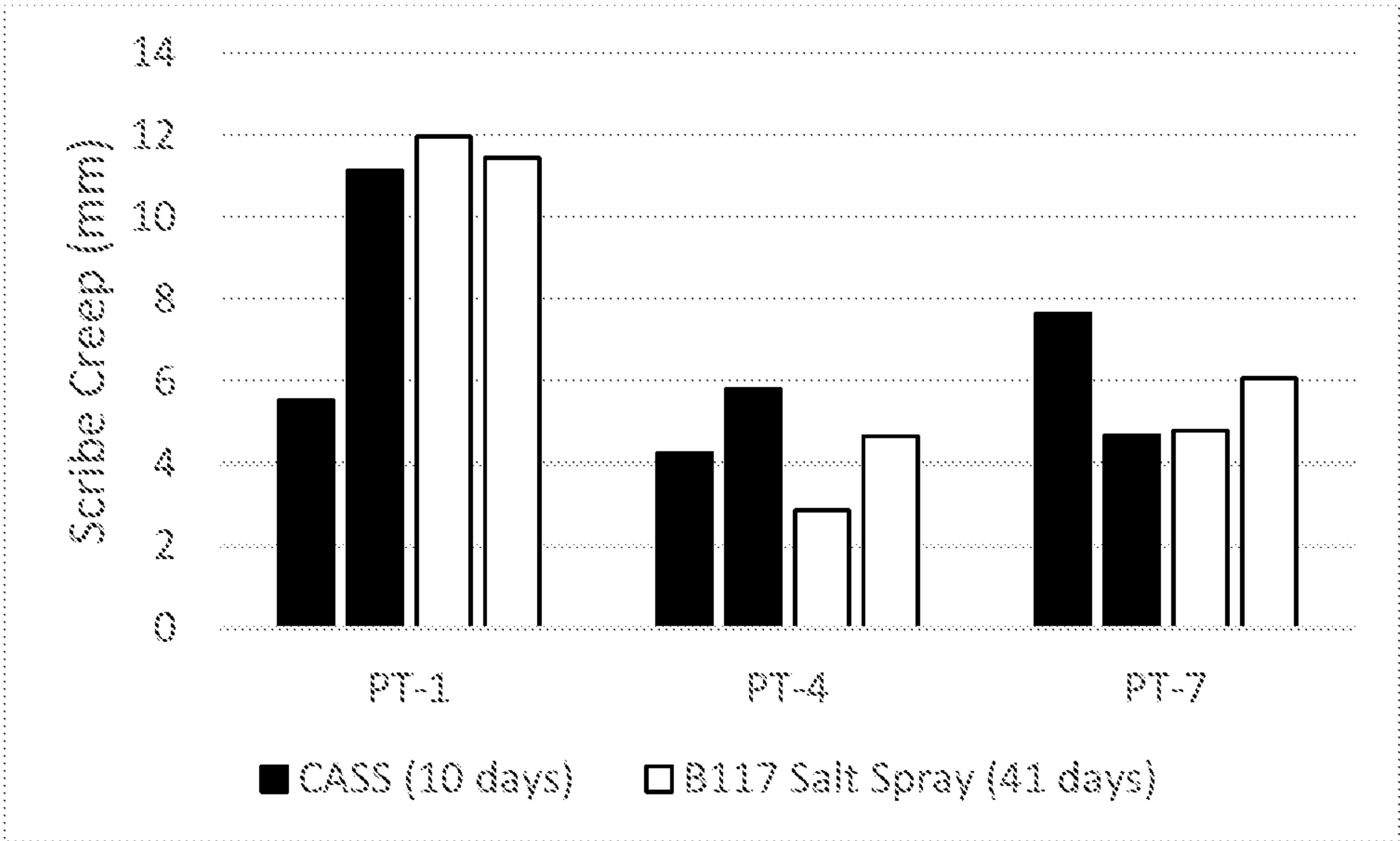


FIG. 7B

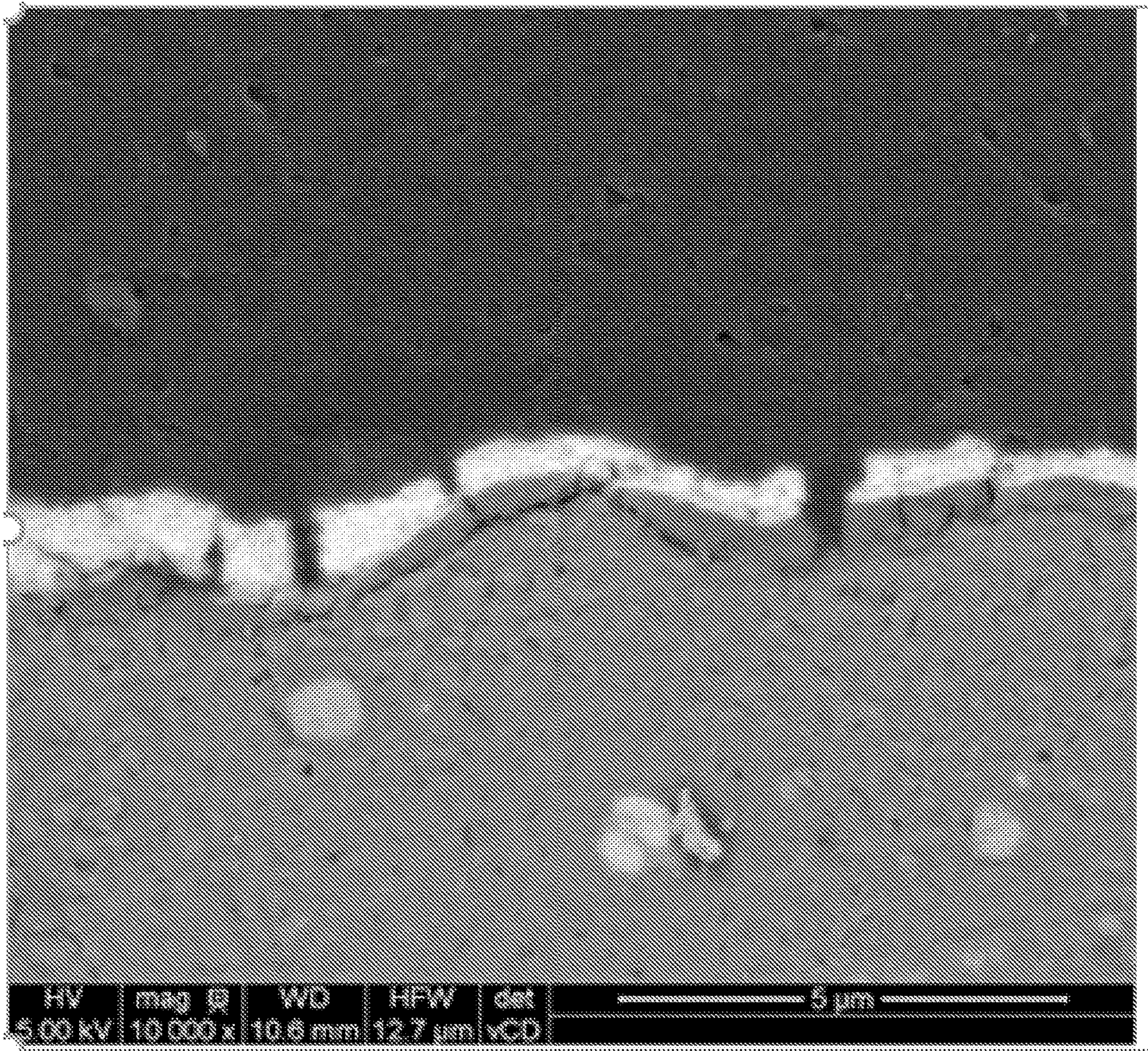


FIG. 7C

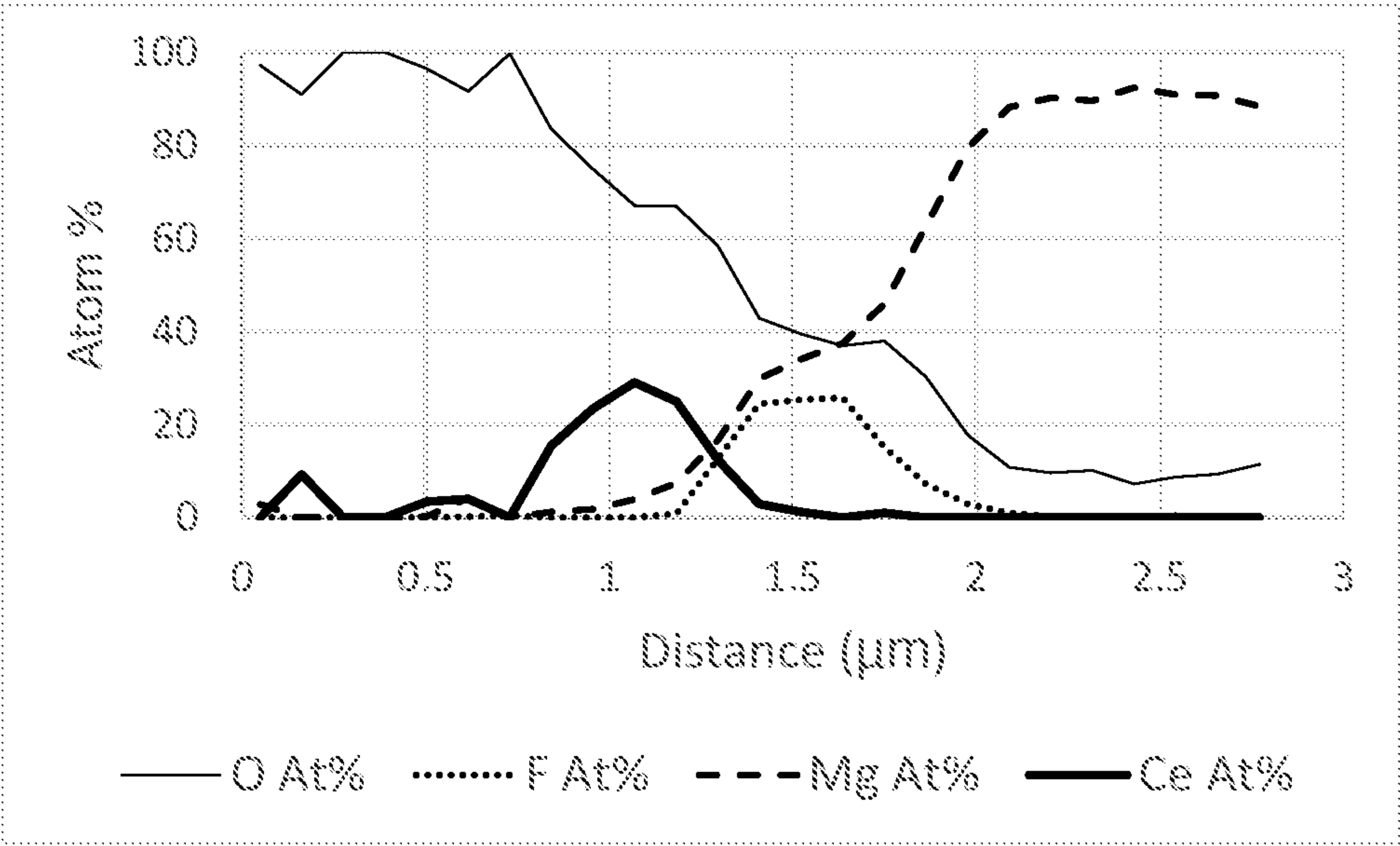


FIG. 7D

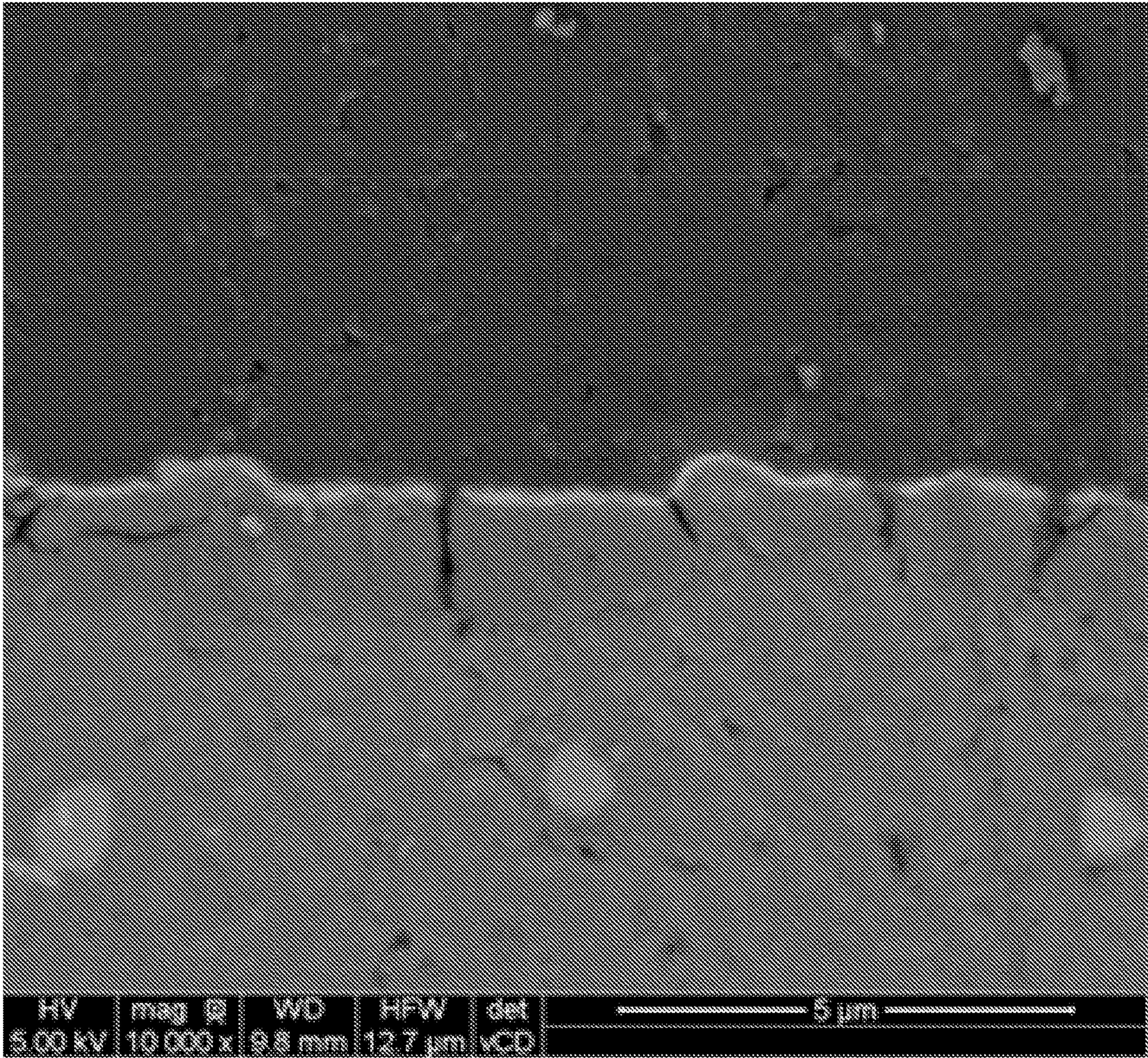


FIG. 7E

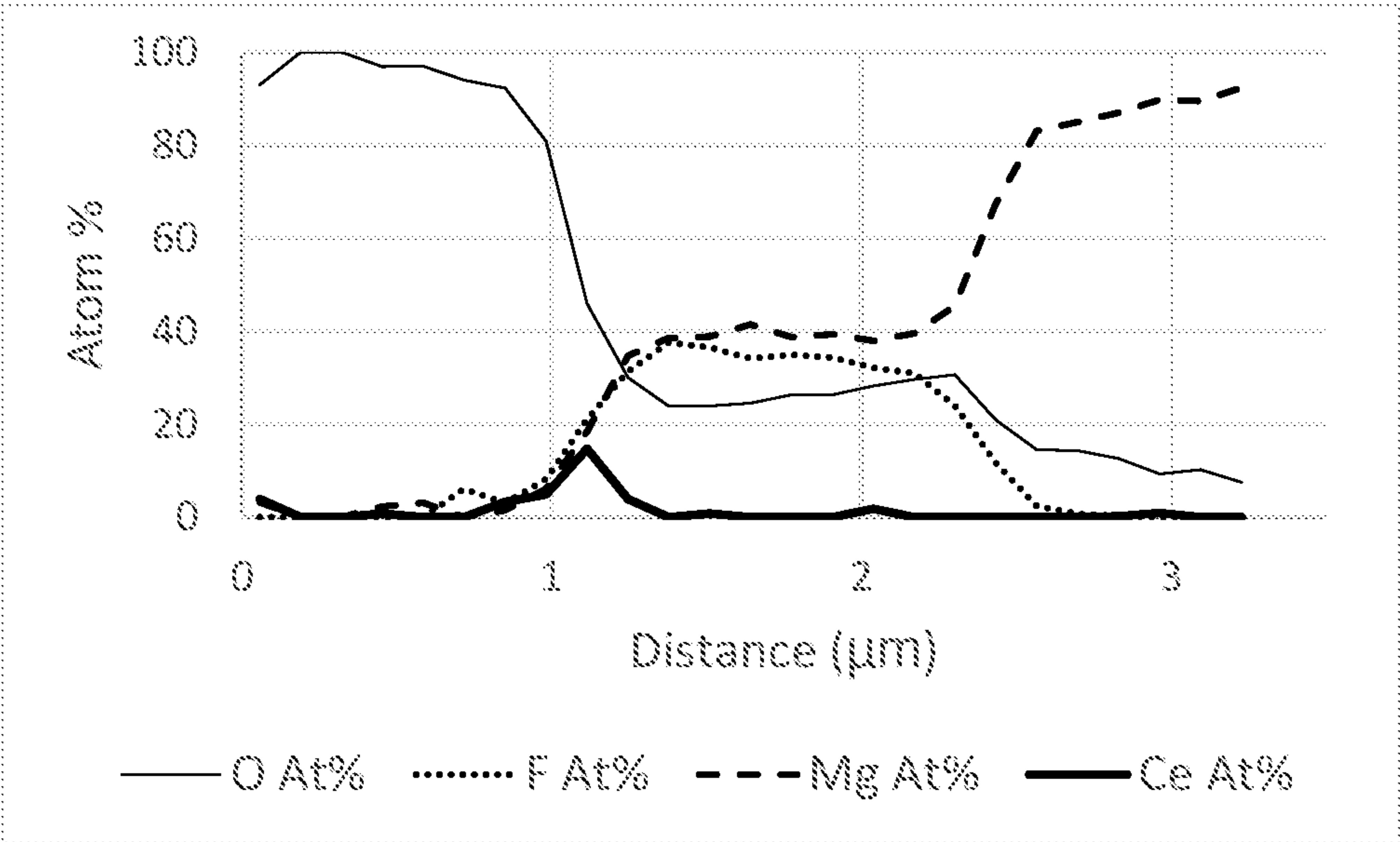


FIG. 7F

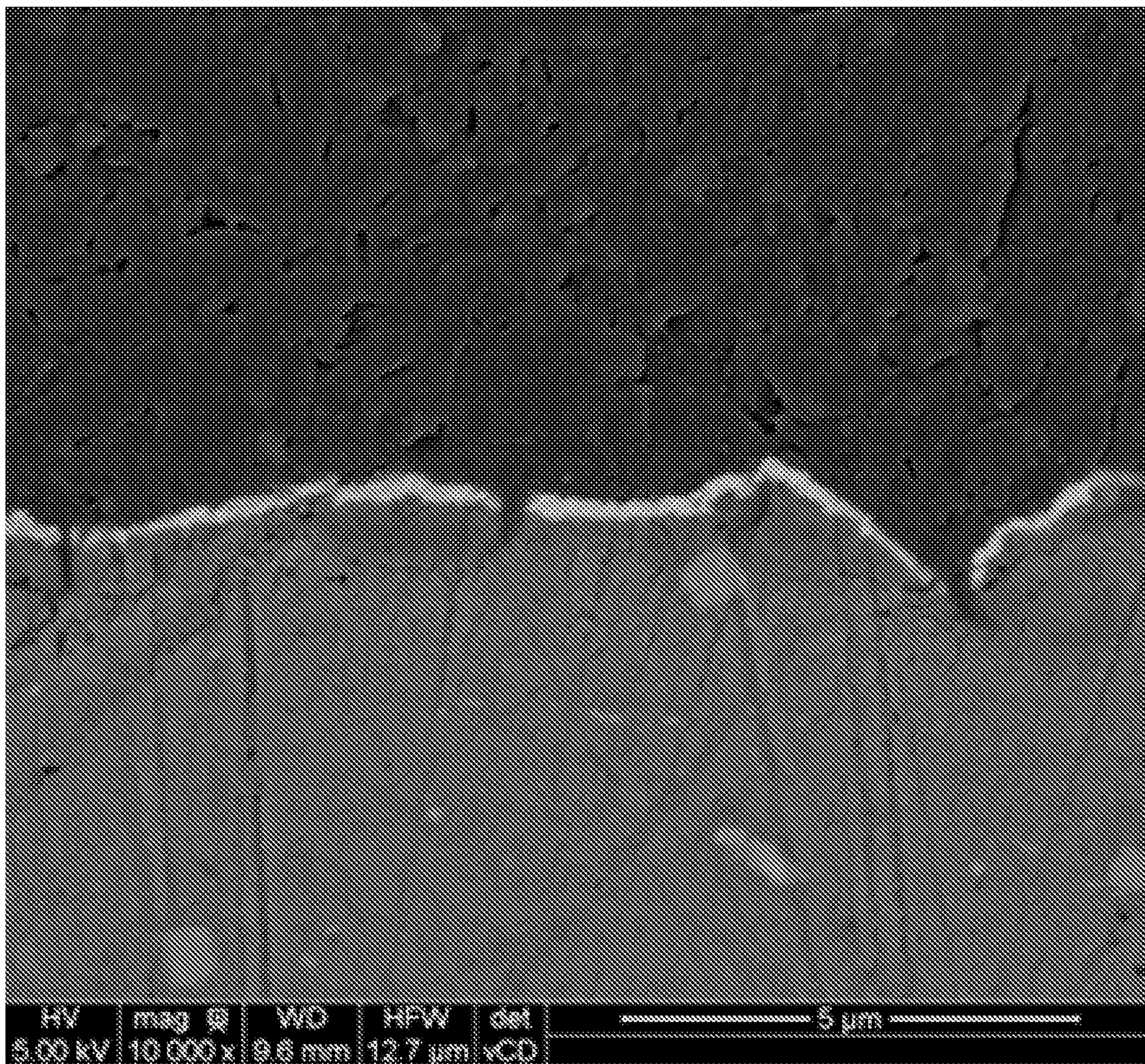


FIG. 7G

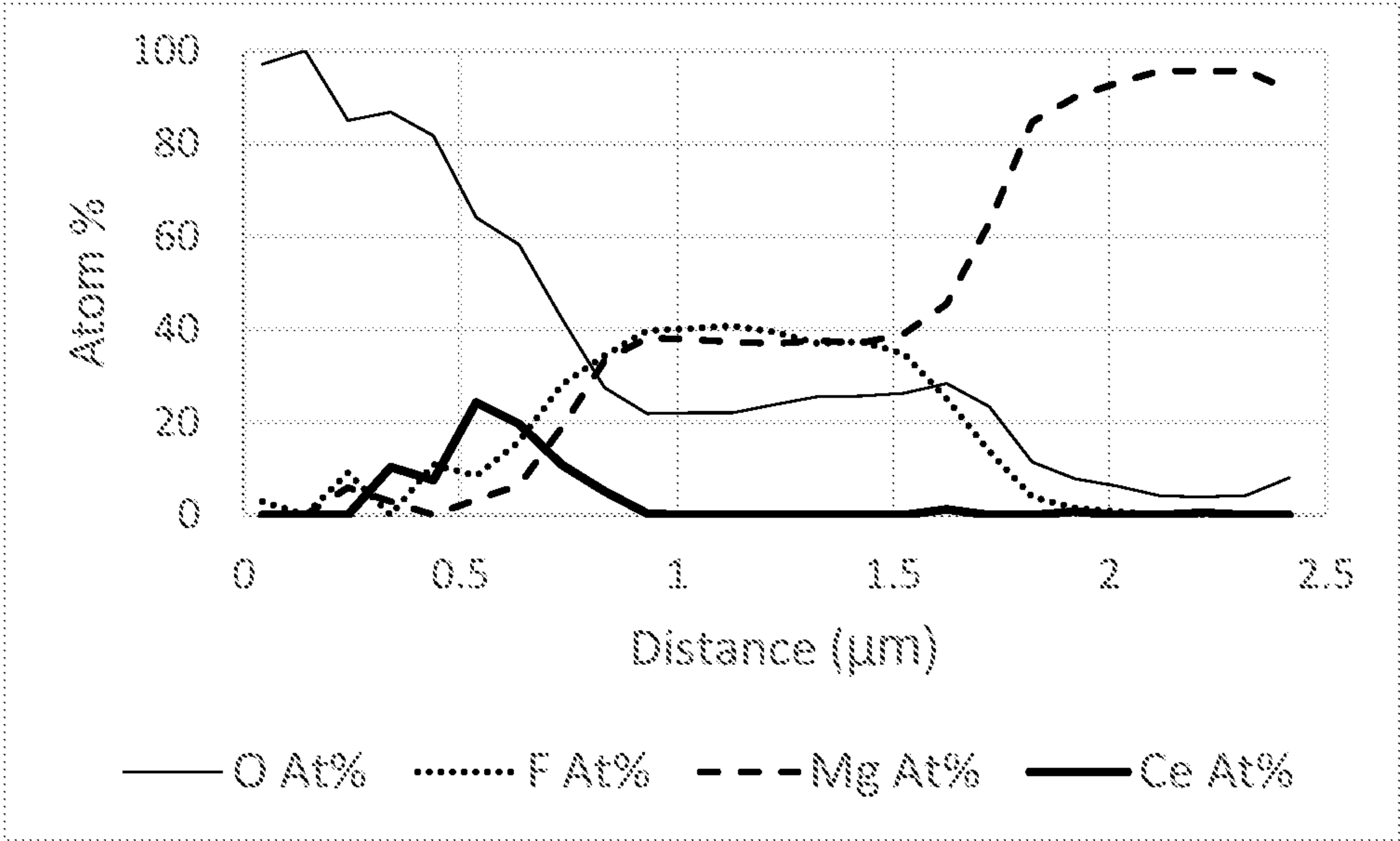


FIG. 7H

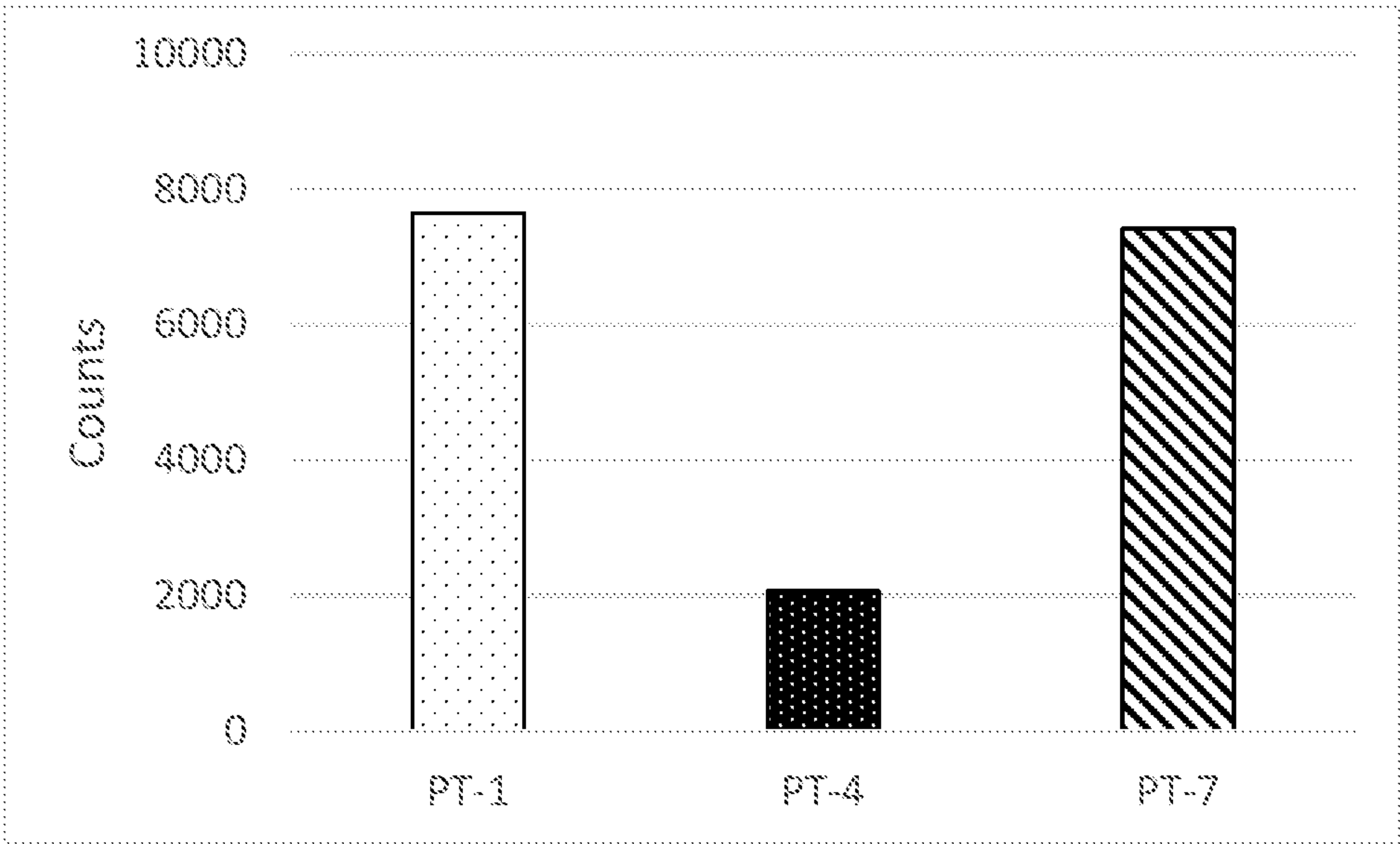


FIG. 8A

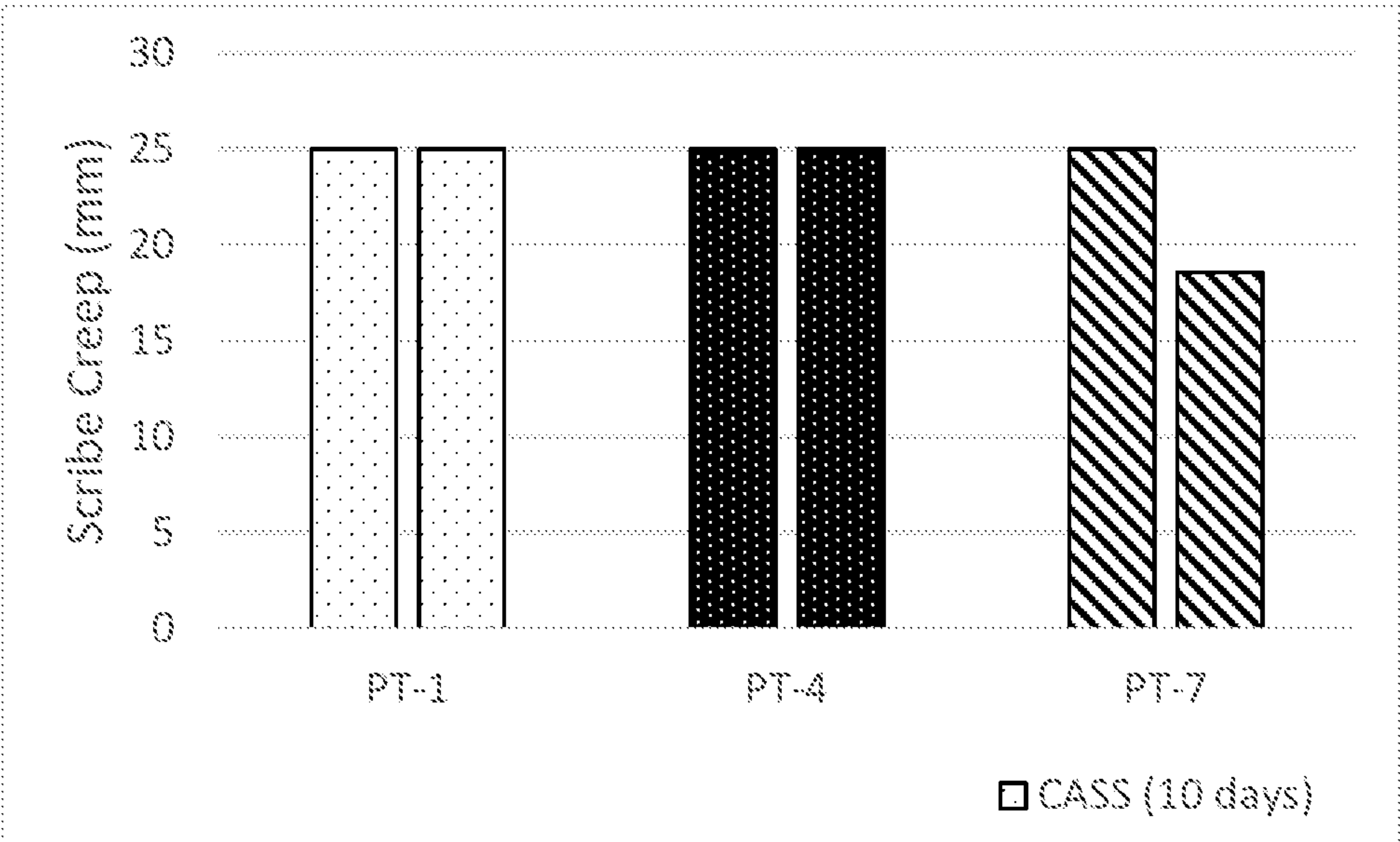


FIG. 8B

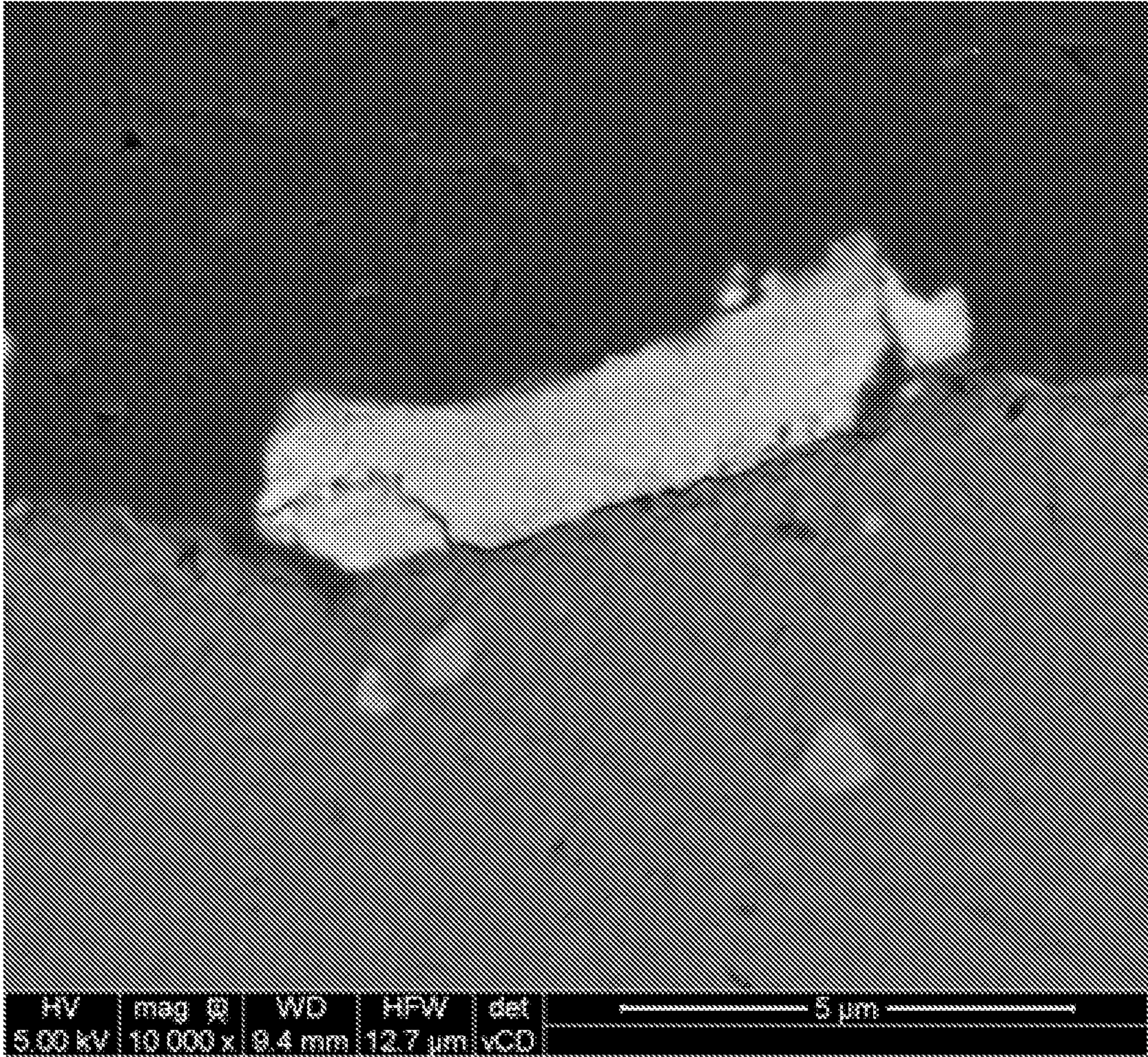


FIG. 8C

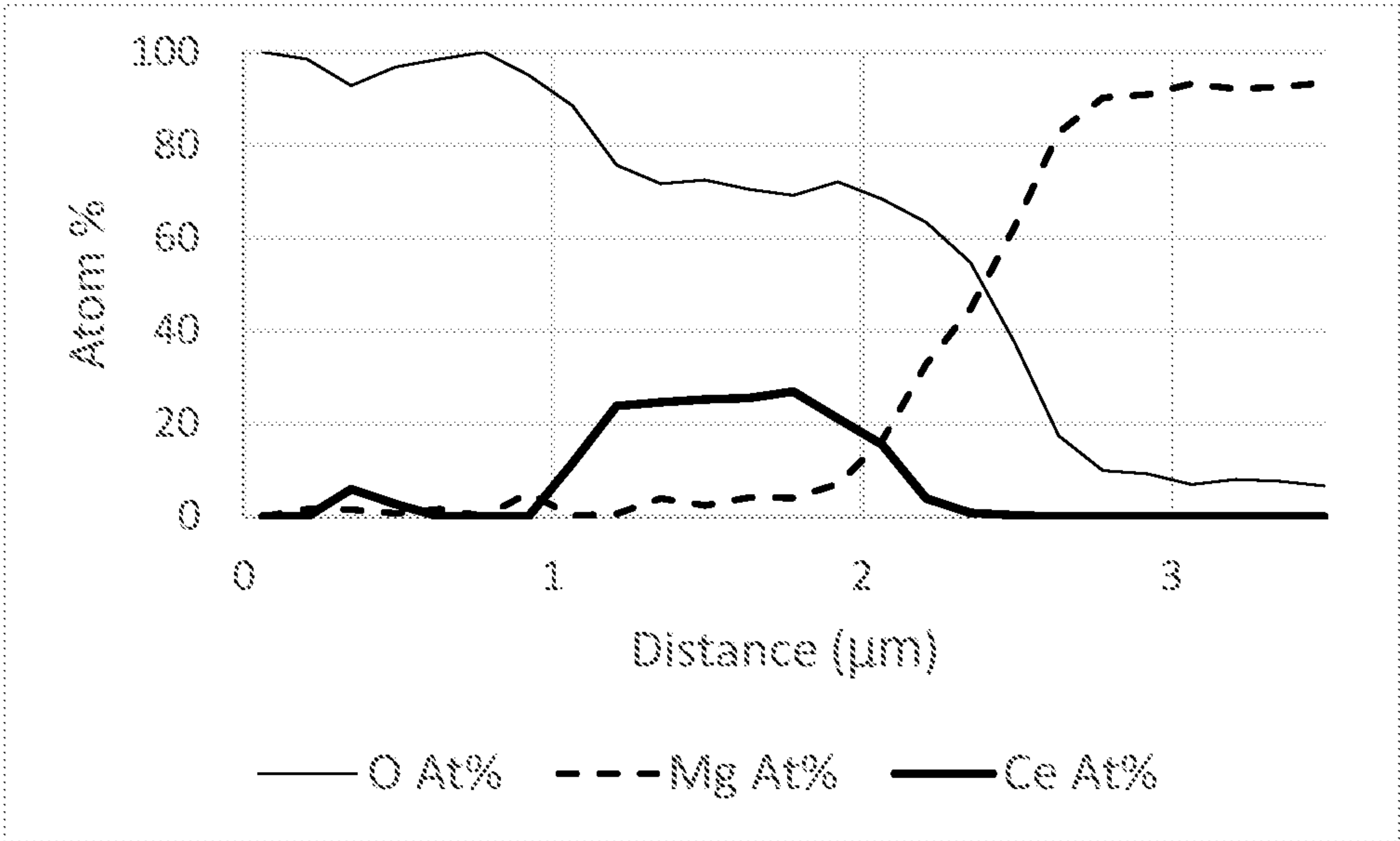


FIG. 8D

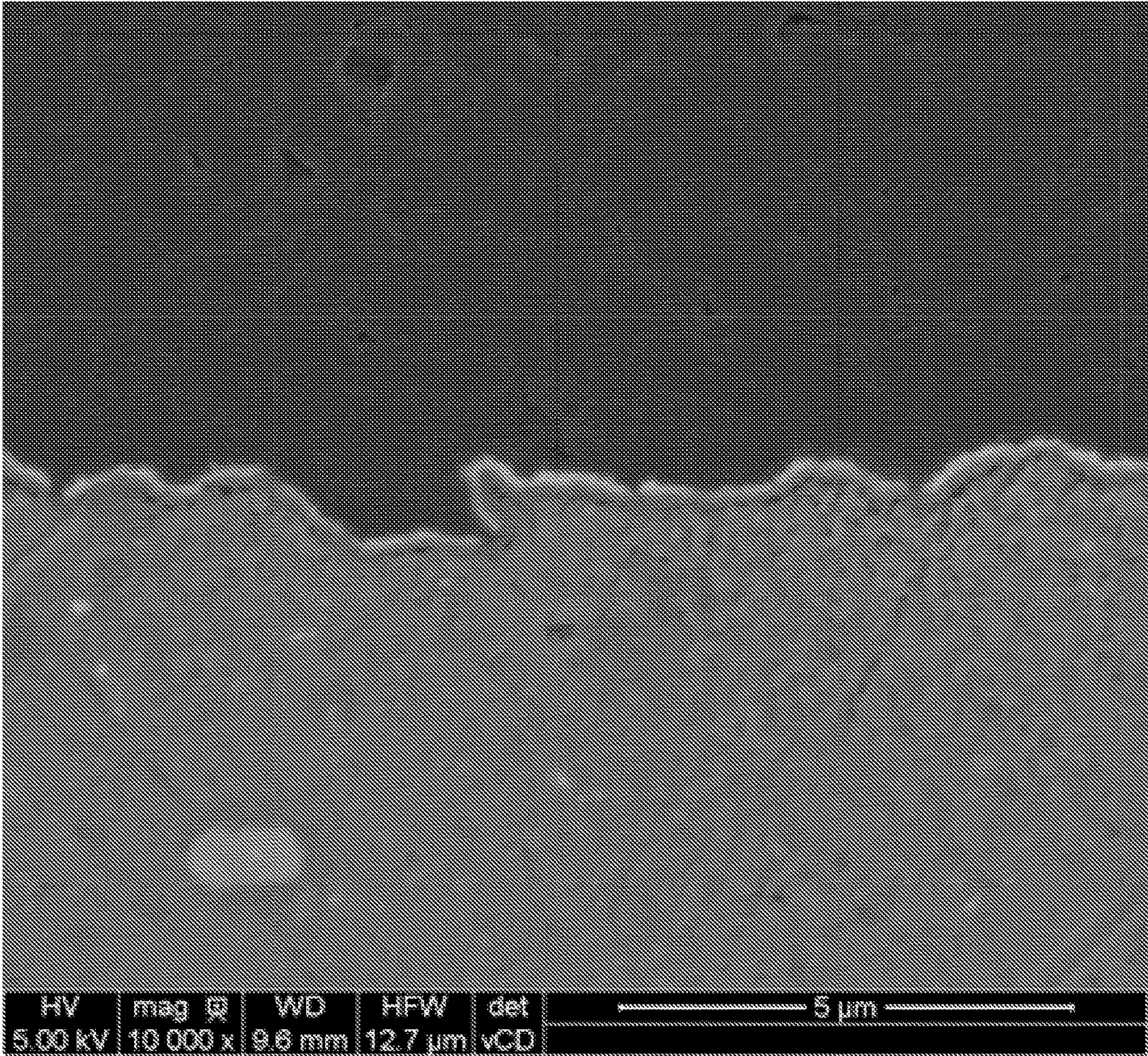


FIG. 8E

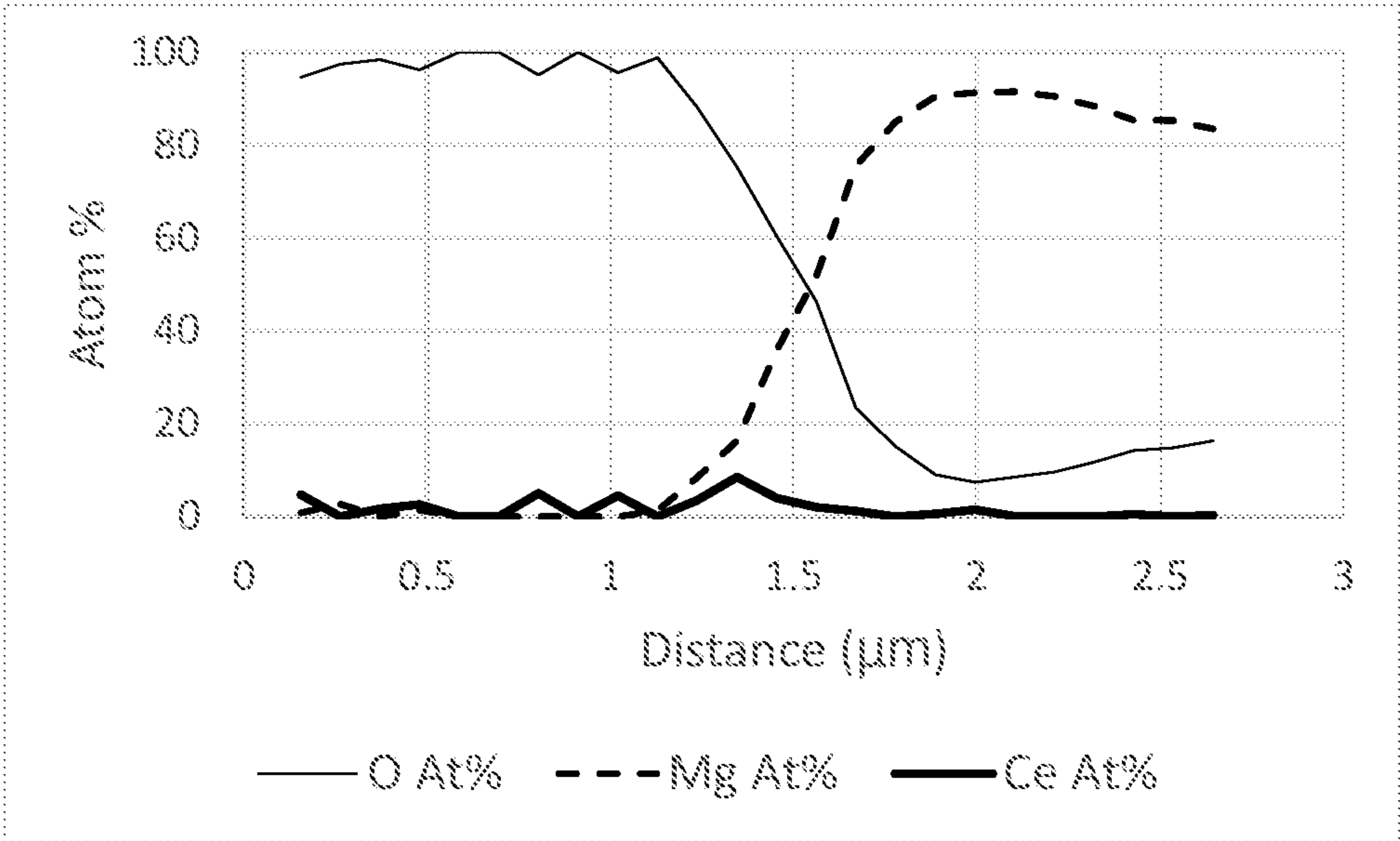


FIG. 8F

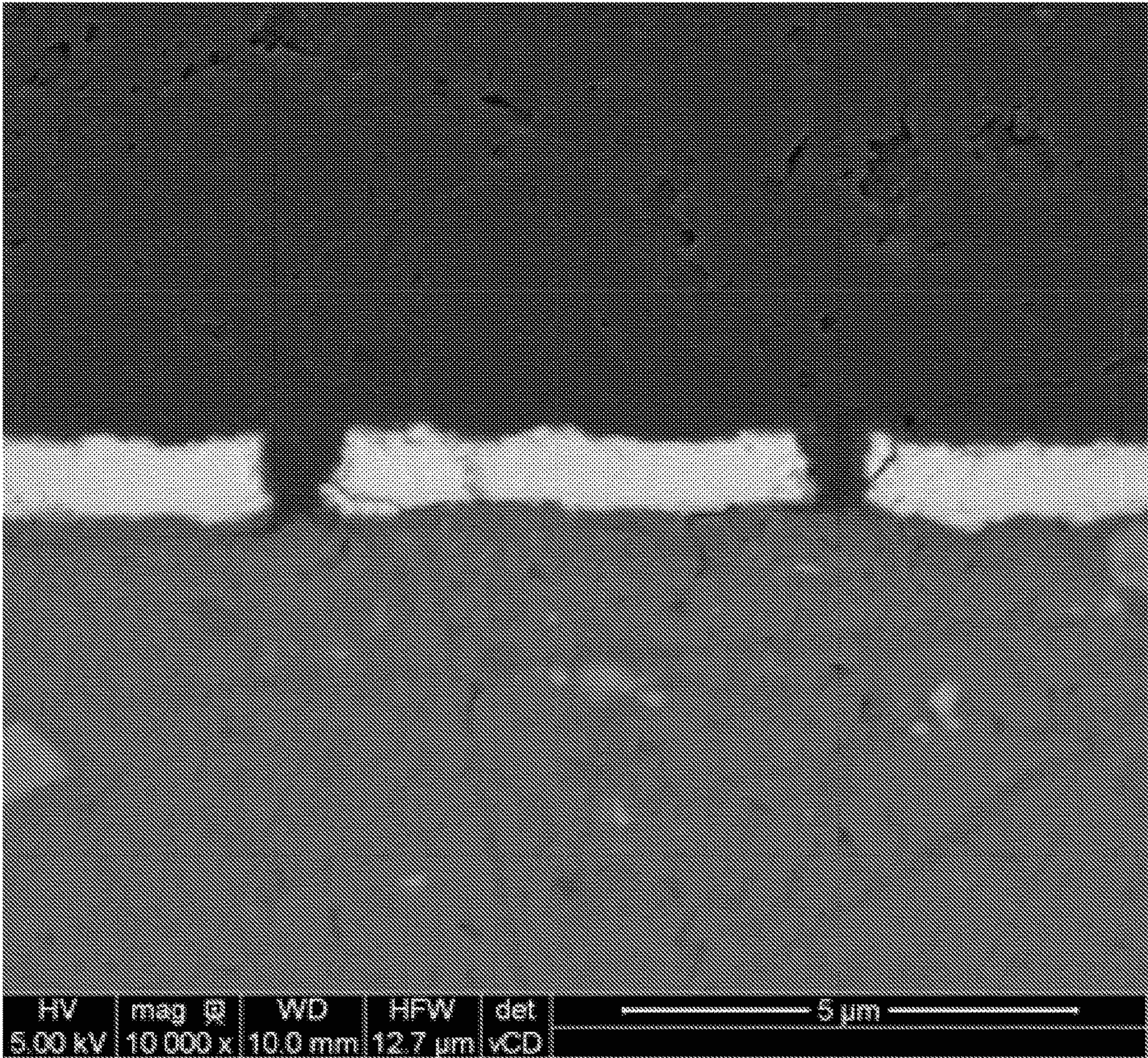


FIG. 8G

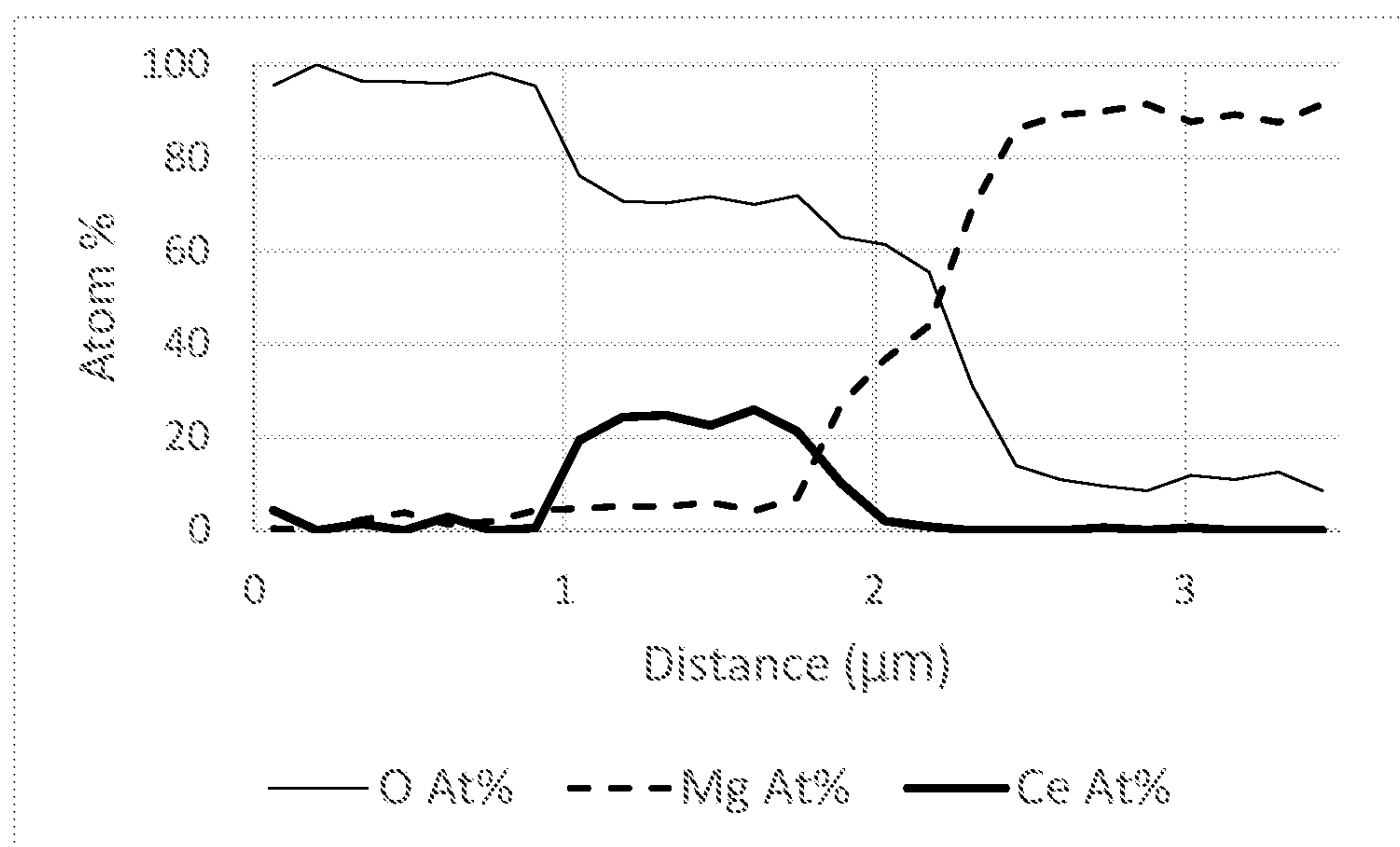


FIG. 8H

SYSTEMS AND METHODS FOR TREATING A SUBSTRATE

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Provisional Patent Application Ser. No. 63/163,387, filed on Mar. 19, 2021, and entitled “Systems and Methods for Treating a Substrate,” incorporated in its entirety herein by reference.

GOVERNMENT CONTRACT

[0002] This material is based upon work supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy under Cooperative Agreement DE-EE0007756 entitled U.S. Automotive Materials Partnership Low-Cost Mg Sheet Component Development and Demonstration Project.

FIELD OF THE INVENTION

[0003] The present invention relates to compositions, systems, and methods for treating a substrate.

BACKGROUND OF THE INVENTION

[0004] The use of protective coatings on metal substrates for improved corrosion resistance and paint adhesion is common. Conventional techniques for coating such substrates include techniques that involve pretreating the metal substrate with chromium-containing compositions. The use of such chromate-containing compositions, however, imparts environmental and health concerns.

SUMMARY OF THE INVENTION

[0005] Disclosed herein is a system for treating a magnesium or a magnesium alloy substrate comprising: a first pretreatment composition comprising a fluorometallic acid and free fluoride in an amount of 10 ppm to 500 ppm based on total weight of the first pretreatment composition and having a pH of 1.0 to 4.0; and a second pretreatment composition comprising a lanthanide series metal, the second pretreatment composition being substantially free of peroxide.

[0006] Also disclosed herein is a method of treating a magnesium or a magnesium alloy substrate comprising: contacting at least a portion of a surface of the substrate with a first pretreatment composition comprising a fluorometallic acid and free fluoride in an amount of 10 ppm to 500 ppm based on total weight of the first pretreatment composition and having a pH of 1.0 to 4.0; and contacting at least a portion of the substrate surface with a second pretreatment composition comprising a lanthanide series metal and being substantially free of peroxide.

[0007] Also disclosed herein is a magnesium or magnesium alloy substrate, wherein (a) a lanthanide series metal is present in an amount of at least 500 counts as measured by X-ray fluorescence (measured using an X-Met 755, Oxford Instruments; operating parameters 60 second timed assay, 15 Kv, 45 μ A, filter 3, T(p)=1.1 μ s); (b) aluminum is present in an amount of at least 150 counts as measured by X-ray fluorescence (measured using an X-Met 755, Oxford Instruments; operating parameters 60 second timed assay, 15 Kv, 45 μ A, K α line, T(p)=1.1 μ s); (c) a lanthanide series metal is present between an air/substrate interface and 1 m below

the air/substrate interface in an amount of no more 25 atomic % as measured by an EDX line scan collected from a surface of the substrate to the bulk of the substrate in cross-section with a 5.00 kV accelerating voltage and a 3.0 spot size; and/or (d) oxygen is present between the air/substrate interface and 1 m below the air/substrate interface in an amount of more than 65 atomic % as measured by an EDX line scan collected from a surface of the substrate to the bulk of the substrate in cross-section with a 5.00 kV accelerating voltage and a 3.0 spot size.

[0008] Also disclosed herein is a treated magnesium or magnesium alloy substrate comprising a surface, wherein at least a portion of the surface is treated with one of the systems or methods of the present invention.

[0009] Also disclosed are magnesium and magnesium alloy substrates comprising a surface at least partially coated with a layer formed from one of the compositions disclosed herein.

BRIEF DESCRIPTION OF THE FIGURES

[0010] FIG. 1 shows data from panels treated in Example 1 with spontaneously deposited pretreatment compositions. Panel (A) is a bar graph showing the deposition of cerium (counts) measured using X-ray fluorescence (XRF), Panel (B) is a bar graph showing the scribe creep, Panel (C) is a scanning electron microscope (SEM) image of a panel treated with PTMT I and PT-1, Panel (D) is a line profiling of the SEM image shown in FIG. 1C, Panel (E) is an SEM image of a panel treated with PTMT I and PT-4, and Panel (F) is a line profiling of the SEM image shown in FIG. 1E.

[0011] FIG. 2 shows data from panels treated in Example 2 with spontaneously deposited pretreatment compositions. Panel (A) is a bar graph showing the deposition of cerium (counts) measured using XRF and Panel (B) is a bar graph showing the scribe creep.

[0012] FIG. 3 shows data from panels treated in Example 3 with spontaneously deposited pretreatment compositions. Panel (A) is a bar graph showing the deposition of cerium (counts) measured using XRF, Panel (B) is a bar graph showing the scribe creep, Panel (C) is an SEM of a panel treated with PT-1, and Panel (D) is a line profiling of the SEM image shown in FIG. 3C.

[0013] FIG. 4 shows data from panels treated in Example 4 with spontaneously deposited pretreatment compositions. Panel (A) is a bar graph showing the deposition of cerium (counts) measured using XRF and Panel (B) is a bar graph showing the scribe creep.

[0014] FIG. 5 shows data from panels treated in Example 5 with spontaneously deposited pretreatment compositions. Panel (A) is a bar graph showing the deposition of cerium (counts) measured using XRF, Panel (B) is a bar graph showing the scribe creep, and Panel (C) is a bar graph showing dry adhesion and wet adhesion of coatings to treated panels. Panel (D) shows exemplary panels for each rating 1-10 on the rating scale used for adhesion testing.

[0015] FIG. 6 shows data from panels treated in Example 6 with spontaneously deposited pretreatment compositions. Panel (A) is a bar graph showing the deposition of cerium (counts) measured using XRF and Panel (B) is a bar graph showing the scribe creep.

[0016] FIG. 7 shows data from panels treated in Example 7 with electrodeposited pretreatment compositions. Panel (A) is a bar graph showing the deposition of cerium (counts) measured using XRF and Panel (B) is a bar graph showing

the scribe creep, Panel (C) is an SEM of a panel treated with Pretreatment PTMT I and PT-1, Panel (D) is a line profiling of the SEM image shown in FIG. 7C, Panel (E) is an SEM image of a panel treated with Pretreatment PTMT I and PT-4, Panel (F) is a line profiling of the SEM image shown in FIG. 7E, Panel (G) is an SEM image of a panel treated with Pretreatment PTMT I and PT-7, and Panel (H) is a line profiling of the SEM image shown in FIG. 7G.

[0017] FIG. 8 shows data from panels treated in Example 8 with electrodeposited pretreatment compositions. Panel (A) is a bar graph showing the deposition of cerium (counts) measured using XRF, Panel (B) is a bar graph showing the scribe creep, Panel (C) is an SEM of a panel treated with PT-1, Panel (D) is a line profiling of the SEM image shown in FIG. 8C, Panel (E) is an SEM of a panel treated with PT-4, Panel (F) is a line profiling of the SEM image shown in FIG. 8E, Panel (G) is an SEM of a panel treated with PT-7, and Panel (H) is a line profiling of the SEM image shown in FIG. 8G.

DETAILED DESCRIPTION OF THE INVENTION

[0018] For purposes of the following detailed description, it is to be understood that the invention may assume various alternative variations and step sequences, except where expressly specified to the contrary. Moreover, other than in any operating examples, or where otherwise indicated, all numbers such as those expressing values, amounts, percentages, ranges, subranges and fractions may be read as if prefaced by the word “about,” even if the term does not expressly appear. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Where a closed or open-ended numerical range is described herein, all numbers, values, amounts, percentages, subranges and fractions within or encompassed by the numerical range are to be considered as being specifically included in and belonging to the original disclosure of this application as if these numbers, values, amounts, percentages, subranges and fractions had been explicitly written out in their entirety.

[0019] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard variation found in their respective testing measurements.

[0020] As used herein, unless indicated otherwise, a plural term can encompass its singular counterpart and vice versa, unless indicated otherwise. For example, although reference is made herein to “a” Group IVA metal and “a” urea compound, a combination (i.e., a plurality) of these components can be used.

[0021] In addition, in this application, the use of “or” means “and/or” unless specifically stated otherwise, even though “and/or” may be explicitly used in certain instances.

[0022] As used herein, “including,” “containing” and like terms are understood in the context of this application to be synonymous with “comprising” and are therefore open-ended and do not exclude the presence of additional undescribed or unrecited elements, materials, ingredients or method steps. As used herein, “consisting of” is understood in the context of this application to exclude the presence of any unspecified element, ingredient or method step. As used herein, “consisting essentially of” is understood in the context of this application to include the specified elements, materials, ingredients or method steps “and those that do not materially affect the basic and novel characteristic(s)” of what is being described.

[0023] As used herein, the terms “on,” “onto,” “applied on,” “applied onto,” “formed on,” “deposited on,” “deposited onto,” mean formed, overlaid, deposited, or provided on but not necessarily in contact with the surface. For example, a coating composition “applied onto” a substrate does not preclude the presence of one or more other intervening coating layers of the same or different composition located between the coating composition and the substrate.

[0024] As used herein, a “system” refers to a plurality of treatment compositions (including cleaners and rinses) used to treat a substrate and to produce a treated substrate. The system may be part of a production line (such as a factory production line) that produces a finished substrate or a treated substrate that is suitable for use in other production lines. As used herein, reference to a “first pretreatment composition” and a “second pretreatment composition” is not intended to imply any specific order of treatment but rather is for ease of reference only.

[0025] As used herein, a “salt” refers to an ionic compound made up of metal cations and non-metallic anions and having an overall electrical charge of zero. Salts may be hydrated or anhydrous.

[0026] As used herein, “aqueous composition” refers to a solution or dispersion in a medium that comprises predominantly water. For example, the aqueous composition may comprise water in an amount of more than 50 wt. %, or more than 70 wt. % or more than 80 wt. % or more than 90 wt. % or more than 95 wt. % based on the total weight of the aqueous composition. That is, the aqueous composition may for example consist substantially of water.

[0027] As used herein, the term “dispersion” refers to a two-phase transparent, translucent or opaque system in which non-soluble particles are in the dispersed phase and an aqueous medium, which includes water, is in the continuous phase.

[0028] As used herein, “deoxidizing composition” or “deoxidizer” refers to a composition that etches the metal substrate surface by removing an oxide layer from the surface, wherein such oxide layer may be a passive layer or may be a layer formed as a result of metallurgical processes such as welding, cutting, laser processing, and the like.

[0029] As used herein, “deoxidizing bath” refers to an aqueous bath containing a deoxidizing composition and that may contain components that are byproducts of the process.

[0030] As used herein, “pretreatment composition” refers to a composition that is capable of reacting with and chemically altering the substrate surface and binding to it to form a film that affords corrosion protection.

[0031] As used herein, “pretreatment bath” refers to an aqueous bath containing the pretreatment composition and that may contain components that are byproducts of the process.

[0032] As used herein, the terms “Group IVA metal” and “Group IVA element” refer to an element that is in group IVA of the CAS version of the Periodic Table of the Elements as is shown, for example, in the Handbook of Chemistry and Physics, 63rd edition (1983), corresponding to Group 14 in the actual IUPAC numbering.

[0033] As used herein, the terms “Group IVA metal compound” refer to compounds that include at least one element that is in Group IVA of the CAS version of the Periodic Table of the Elements.

[0034] As used herein, the terms “Group IVB metal” and “Group IVB element” refer to an element that is in group IVB of the CAS version of the Periodic Table of the Elements as is shown, for example, in the Handbook of Chemistry and Physics, 63rd edition (1983), corresponding to Group 4 in the actual IUPAC numbering.

[0035] As used herein, the term “Group IVB metal compound” refers to compounds that include at least one element that is in Group IVB of the CAS version of the Periodic Table of the Elements.

[0036] As used herein, the terms “Group IIIA metal” and “Group IIIA element” refer to an element that is in Group IIIA of the CAS version of the Periodic Table of the Elements as is shown, for example, in the Handbook of Chemistry and Physics, 63rd edition (1983), corresponding to Group 13 in the actual IUPAC system.

[0037] As used herein, the term “Group IIIA metal compound” refers to compounds that include at least one element that is in Group IIIA of the CAS version of the Periodic Table of the Elements.

[0038] As used herein, the terms “Group VIIIB metal” and “Group VIIIB element” refer to an element that is in Group VIIIB of the CAS version of the Periodic Table of the Elements as is shown, for example, in the Handbook of Chemistry and Physics, 63rd edition (1983), corresponding to Group 8 in the actual IUPAC system.

[0039] As used herein, the term “Group VIIIB metal compound” refers to compounds that include at least one element that is in Group VIIIB of the CAS version of the Periodic Table of the Elements.

[0040] As used herein, “urea” refers to an organic compound having the chemical formula $\text{CO}(\text{NH}_2)_2$.

[0041] As used herein, a “coating composition” refers to a composition, e.g., a solution, mixture, or a dispersion, that, in an at least partially dried or cured state, is capable of producing a film, layer, or the like on at least a portion of a substrate surface.

[0042] As used herein, a “system” refers to a plurality of treatment compositions (including cleaners and rinses) used to treat a substrate and to produce a treated substrate. The system may be part of a production line (such as a factory production line) that produces a finished substrate or a treated substrate that is suitable for use in other production lines. As used herein, reference to a “first pretreatment composition,” a “second pretreatment composition,” and a “third pretreatment composition” is not intended to imply any specific order of treatment but rather is for ease of reference only.

[0043] As further defined herein, ambient conditions generally refer to room temperature and humidity conditions or

temperature and humidity conditions that are typically found in the area in which the coating composition is being applied to a substrate, e.g., at 10° C. to 40° C. and 5% to 80% relative humidity, while slightly thermal conditions are temperatures that are slightly above ambient temperature but are generally below the curing temperature for the coating composition (i.e. in other words, at temperatures and humidity conditions below which the reactive components will readily react and cure, e.g., >40° C. and less than 100° C. at 5% to 80% relative humidity).

[0044] As used herein, unless indicated otherwise, the term “substantially free” means that a particular material is only present in a mixture or a composition (or a coating, film or layer formed therefrom) in an amount of less than 5 parts per million (ppm) based on total weight of the mixture or composition (or coating, film, or layer formed therefrom). As used herein, unless indicated otherwise, the term “essentially free” means that a particular material is only present in a mixture or a composition (or a coating, film or layer formed therefrom) in an amount of less than 1 ppm based on total weight of the mixture or composition (or coating, film, or layer formed therefrom). As used herein, unless indicated otherwise, the term “completely free” means that a particular material is only present in a mixture or a composition (or a coating, film or layer formed therefrom) in an amount of less than 1 part per billion (ppb) based on total weight of the mixture or composition (or coating, film, or layer formed therefrom) or that such material is below the detection limit of common analytical techniques. When a mixture or a composition (or a coating, film, or layer formed therefrom) is substantially free, essentially free, or completely free of a particular material, this means that such material in any form is excluded from the mixture or composition (or coating, film, or layer formed therefrom), this means that such material in any form is excluded from the mixture or composition (or coating, film, or layer formed therefrom), except that such material may unintentionally be present as a result of, for example, carry-over from prior treatment baths in the processing line, contamination from a substrate, or the like.

[0045] Unless otherwise disclosed herein, as used herein, the terms “total composition weight”, “total weight of a composition” or similar terms refer to the total weight of all ingredients being present in the respective composition including any carriers and solvents.

[0046] As mentioned above, the present invention is directed to a system for treating a metal substrate, the system comprising, or consisting essentially of, or consisting of, (a) a first pretreatment composition and (b) a second pretreatment composition. The first pretreatment composition comprises, or consists essentially of, or consists of, a fluorometallic acid and free fluoride in an amount of 10 ppm to 500 ppm based on total weight of the first pretreatment composition and may have a pH of 1.0 to 4.0. The second pretreatment composition comprises, or consists essentially of, or consists of, a lanthanide series metal and may be substantially free, or essentially free, or completely free, of peroxide. As used herein, “peroxide” refers to a compound having the structure $\text{R}^1\text{—O—O—R}^2$, wherein the oxygen atoms in the O—O group (the “peroxide group”) have an oxidation state of −1 and wherein R^1 and R^2 may be the same or different and may be hydrogen, an inorganic atom, a hydrocarbon and/or a heteroatom containing a hydrocarbon.

[0047] The present invention also is directed to a method of treating a metal substrate. The method may comprise, or may consist essentially of, or may consist of, contacting at least a portion of the substrate surface with one of the first compositions described herein. The method may further comprise, or may consist essentially of, or may consist of, contacting at least a portion of the substrate surface with one of the second compositions described herein. As described more fully herein, in some instances, there may be rinse steps that intervene the contacting with the first composition and the second composition.

Substrates

[0048] Suitable substrates that may be used include magnesium and magnesium alloys of the AZXX (including Eform Plus), AMXX, EVXX, ZKXX, ZEXX, ZCXX, HKXX, HZXX, QEXX, QHXX, WEXX, ZEK100, or Elektron 21 series. In examples, the substrate may comprise at least 50% by weight magnesium based on total weight of the substrate, such as at least 60% by weight magnesium, such as at least 70% by weight magnesium, such as at least 80% by weight magnesium, such as at least 90% by weight magnesium, such as 100% magnesium. Alloy metals may include, for example, aluminum, zinc, neodymium, manganese, silicon, calcium, copper, and/or zirconium. Alloy metals may be present in a total amount of less than 50% by weight based on total weight of the substrate, such as less than 40% by weight, such as less than 30% by weight, such as less than 20% by weight, such as less than 10% by weight, such as less than 5% by weight. For example, the magnesium alloy substrate may comprise zinc present in an amount in an amount of less than 2% by weight based on total weight of the substrate, neodymium may be present in an amount of less than 1% by weight based on total weight of the substrate, and zirconium may be present in an amount of less than 1% by weight based on total weight of the substrate. In another example, the magnesium alloy substrate may comprise aluminum present in an amount of less than 3% by weight by weight based on total weight of the substrate, zinc in an amount of less than 2% by weight based on total weight of the substrate, calcium in an amount of less than 1% by weight based on total weight of the substrate, and manganese in an amount of less than 1% by weight based on total weight of the substrate.

[0049] Suitable substrates for use in the present invention include those that are often used in the assembly of vehicular bodies (e.g., without limitation, door, body panel, trunk deck lid, roof panel, hood, roof and/or stringers, rivets, landing gear components, and/or skins used on an aircraft), a vehicular frame, vehicular parts, motorcycles, wheels, industrial structures and components such as appliances, including washers, dryers, refrigerators, stoves, dishwashers, and the like, personal electronics, agricultural equipment, lawn and garden equipment, air conditioning units, heat pump units, heat exchangers, lawn furniture, and other articles. As used herein, “vehicle” or variations thereof includes, but is not limited to, civilian, commercial, and military aircraft, and/or land vehicles such as cars, motorcycles, and/or trucks. The metal substrate also may be in the form of, for example, a sheet of metal or a fabricated part.

[0050] In examples, the substrate may be a multi-metal article. As used herein, the term “multi-metal article” refers to (1) an article that has at least one surface comprised of a first metal and at least one surface comprised of a second

metal that is different from the first metal, (2) a first article that has at least one surface comprised of a first metal and a second article that has at least one surface comprised of a second metal that is different from the first metal, or (3) both (1) and (2).

[0051] In examples, the substrate may comprise a three-dimensional component formed by an additive manufacturing process such as selective laser melting, e-beam melting, directed energy deposition, binder jetting, metal extrusion, and the like. In examples, the three-dimensional component may be a metal and/or resinous component.

First Pretreatment Composition

[0052] As stated above, the first pretreatment composition comprises a fluorometallic acid and free fluoride in an amount of 10 ppm to 500 ppm based on total weight of the first pretreatment composition. The metal of the fluorometallic acid may comprise, for example, a Group IVA, a Group IVB metal, a Group IIIA metal, and/or a Group VIIIB metal.

[0053] The Group IVA metal may, for example, comprise silicon such as silanes, silicas, silicates, and the like. The Group IVA metal may be provided in the first pretreatment composition in the form of specific compounds of the metals, such as their soluble acids and/or salts. Examples of useful compounds include fluorosilicic acid, ammonium and alkali metal fluorosilicates, and the like, including by way of non-limiting example, hexafluorosilicic acid, hexafluorozirconic acid, hexafluorotitanic acid, hexafluoroferric acid, hexafluoroaluminic acid, or combinations thereof.

[0054] The Group IVA metal, if present at all, may be present in the first pretreatment composition in an amount of at least 10 ppm based on total weight of the first pretreatment composition, such as at least 50 ppm, such as at least 100 ppm, and may be present in the first pretreatment composition in an amount of no more than 2,000 ppm based on total weight of the first pretreatment composition, such as no more than 750 ppm, such as no more than 250 ppm. The Group IVA metal, if present at all, may be present in the first pretreatment composition in an amount of 10 ppm to 2,000 ppm based on total weight of the first pretreatment composition, such as 50 ppm to 750 ppm, such as 100 ppm to 250 ppm.

[0055] The Group IVB metal may comprise zirconium, titanium, hafnium, or combinations thereof. For example, the Group IVB metal used in the first pretreatment composition may be a compound of zirconium, titanium, hafnium, or a mixture thereof. Suitable compounds of zirconium include, but are not limited to, hexafluorozirconic acid, alkali metal and ammonium salts thereof, zirconium tetrafluoride, ammonium zirconium carbonate, zirconium carboxylates and zirconium hydroxy carboxylates, such as zirconium acetate, zirconium oxalate, ammonium zirconium glycolate, ammonium zirconium lactate, ammonium zirconium citrate, zirconium basic carbonate, and mixtures thereof. Suitable compounds of titanium include, but are not limited to, fluorotitanic acid and its salts. A suitable compound of hafnium includes, but is not limited to, hafnium nitrate.

[0056] The Group IVB metal, if present at all, may be present in the first pretreatment composition in an amount of at least 200 ppm based on total weight of the first pretreatment composition, such as at least 350 ppm, such as at least 500 ppm. The Group IVB metal, if present at all, may be present in the first pretreatment composition in an amount of

no more than 5,000 ppm based on total weight of the first pretreatment composition, such as no more than 2,500 ppm, such as no more than 1,750 ppm. The Group IVB metal may be present in the first pretreatment composition in a total amount of 200 ppm to 5,000 ppm based on total weight of the first pretreatment composition, such as 350 ppm to 2,500 ppm, such as 500 ppm to 1,750 ppm. In some instances, the composition may comprise more than one type of Group IVB metal. In such instances, each type of Group IVB metal may be present in the amounts disclosed above.

[0057] The first pretreatment composition may further comprise an anion that may be suitable for forming a salt with any of the Group IVA or Group IVB metals described above, such as a silicate (orthosilicates and metasilicates), carbonates, hydroxides, and the like.

[0058] The Group IIIA metal may comprise aluminum, boron, gallium, indium, thallium, or combination thereof. For example, the Group IIIA metal used in the first pretreatment composition may be a compound of aluminum, boron, gallium, indium, thallium, or a mixture thereof.

[0059] The Group IIIA metal may be present in the second composition in an amount of at least 10 ppm based on total weight of the second composition, such as at least 50 ppm, such as at least 100 ppm, and may be present in the second composition in an amount of no more than 1,500 ppm based on total weight of the second composition, such as no more than 750 ppm, such as no more than 500 ppm. The Group IIIA metal may be present in the second composition in an amount of 10 ppm to 1,500 ppm based on total weight of the second composition, such as 50 ppm to 750 ppm, such as 100 ppm to 500 ppm. In such instances, each type of Group IIIA metal may be present in the amounts disclosed above.

[0060] The Group VIII metal may comprise iron. For example, the Group VIII metal used in the first pretreatment composition may be a compound of iron.

[0061] The Group VIIIB metal of the fluorometallic acid may be present in the second composition in an amount of at least 100 ppm based on total weight of the second composition, such as at least 250 ppm, such as at least 300 ppm. The Group VIIIB metal of the fluorometallic acid may be present in the second composition in an amount of no more than 3,000 ppm based on total weight of the second composition, such as no more than 1,500 ppm, such as no more than 3,000 ppm. The Group VIIIB metal of the fluorometallic acid may be present in the second composition in a total amount of 100 ppm to 3,000 ppm based on total weight of the second composition, such as 250 ppm to 1,500 ppm, such as 300 ppm to 1,000 ppm. In such instances, each type of Group VIIIB metal may be present in the amounts disclosed above.

[0062] A source of free fluoride may be present in the first pretreatment composition. The free fluoride may be derived from a compound or complex comprising the Group IVA metal, the Group IVB metal, the Group IIIA metal, and/or the Group VIIIB metal described above and/or may be derived from a compound or complex other than a compound or complex comprising the Group IVA metal, the Group IVB metal, the Group IIIA metal, and/or the Group VIIIB metal, such as, for example, potassium bifluoride or hydrogen fluoride. As used herein the amount of fluoride disclosed or reported in the first pretreatment composition is referred to as “free fluoride,” that is, fluoride present in the first pretreatment composition that is not bound to metal ions or hydrogen ions, as measured in parts per million of

fluoride. Free fluoride is defined herein as being able to be measured using, for example, an Orion Dual Star Dual Channel Benchtop Meter equipped with a fluoride ion selective electrode (“ISE”) available from Thermoscientific, the Symphony® Fluoride Ion Selective Combination Electrode supplied by VWR International, or similar electrodes. See, e.g., Light and Cappuccino, *Determination of fluoride in toothpaste using an ion-selective electrode*, J. Chem. Educ., 52:4, 247-250, April 1975. The fluoride ISE may be standardized by immersing the electrode into solutions of known fluoride concentration and recording the reading in millivolts, and then plotting these millivolt readings in a logarithmic graph. The millivolt reading of an unknown sample can then be compared to this calibration graph and the concentration of fluoride determined. Alternatively, the fluoride ISE can be used with a meter that will perform the calibration calculations internally and thus, after calibration, the concentration of the unknown sample can be read directly.

[0063] The free fluoride of the first pretreatment composition may be present in an amount of at least 10 ppm based on a total weight of the first pretreatment composition, such as at least 25 ppm, such as at least 35 ppm. The free fluoride of the first pretreatment composition may be present in an amount of no more than 500 ppm based on a total weight of the first pretreatment composition, such as no more than 200 ppm such as no more than 100 ppm, such as no more than 75 ppm. The free fluoride of the first pretreatment composition may be present in an amount of 10 ppm free fluoride to 500 ppm free fluoride based on a total weight of the first pretreatment composition, such as 10 ppm to 200 ppm, such as 25 ppm to 100 ppm, 35 ppm to 75 ppm.

[0064] The first pretreatment composition may exclude chromium or chromium-containing compounds. As used herein, the term “chromium-containing compound” refers to materials that include trivalent and/or hexavalent chromium. Non-limiting examples of such materials include chromic acid, chromium trioxide, chromic acid anhydride, dichromate salts, such as ammonium dichromate, sodium dichromate, potassium dichromate, and calcium, barium, magnesium, zinc, cadmium, strontium dichromate, chromium(III) sulfate, chromium(III) chloride, and chromium(III) nitrate. When a first pretreatment composition or a material deposited on a substrate surface by deposition of the first pretreatment composition is substantially free, essentially free, or completely free of chromium, this includes chromium in any form, such as, but not limited to, the trivalent and hexavalent chromium-containing compounds listed above.

[0065] Thus, optionally, the first pretreatment compositions and/or material deposited on a substrate surface by deposition of the first pretreatment composition may be substantially free, may be essentially free, and/or may be completely free of one or more of any of the elements or compounds listed in the preceding paragraph. A first pretreatment composition or a material deposited on a substrate surface by deposition of the first pretreatment composition that is substantially free of chromium or derivatives thereof means that chromium or derivatives thereof are not intentionally added, but may be present in trace amounts, such as because of impurities or unavoidable contamination from the environment. In other words, the amount of material is so small that it does not affect the properties of the first pretreatment composition or deposited material; in the case of chromium, this may further include that the element or

compounds thereof are not present in the first pretreatment compositions and/or deposited material in such a level that it causes a burden on the environment. The term “substantially free” means that the first pretreatment compositions and/or deposited material contain less than 10 ppm of any or all of the elements or compounds listed in the preceding paragraph based on total weight of the composition or the layer, respectively, if any at all. The term “essentially free” means that the first pretreatment compositions and/or deposited material contain less than 1 ppm of any or all of the elements or compounds listed in the preceding paragraph, if any at all. The term “completely free” means that the first pretreatment compositions and/or deposited material contain less than 1 ppb of any or all of the elements or compounds listed in the preceding paragraph, if any at all.

[0066] The first pretreatment composition may, in some instances, exclude phosphate ions or phosphate-containing compounds and/or the formation of sludge, such as aluminum phosphate, iron phosphate, and/or zinc phosphate, formed in the case of using a treating agent based on zinc phosphate. As used herein, “phosphate-containing compounds” include compounds containing the element phosphorous such as ortho phosphate, pyrophosphate, metaphosphate, tripolyphosphate, organophosphonates, and the like, and can include, but are not limited to, monovalent, divalent, or trivalent cations such as: sodium, potassium, calcium, zinc, nickel, manganese, aluminum and/or iron. When a composition and/or a material deposited on a substrate surface by deposition of the first pretreatment composition is substantially free, essentially free, or completely free of phosphate, this includes phosphate ions or compounds containing phosphate in any form.

[0067] Thus, the first pretreatment composition and/or a material deposited on a substrate surface by deposition of the first pretreatment composition may be substantially free, or in some cases may be essentially free, or in some cases may be completely free, of one or more of any of the ions or compounds listed in the preceding paragraph. A first pretreatment composition and/or deposited material is substantially free of phosphate means that phosphate ions or compounds containing phosphate are not intentionally added, but may be present in trace amounts, such as because of impurities or unavoidable contamination from the environment. In other words, the amount of material is so small that it does not affect the properties of the composition; this may further include that phosphate is not present in the first pretreatment compositions and/or deposited materials in such a level that they cause a burden on the environment. The term “substantially free” means that the first pretreatment compositions and/or deposited material contain less than 5 ppm of any or all of the phosphate anions or compounds listed in the preceding paragraph based on total weight of the composition or the deposited material, respectively, if any at all. The term “essentially free” means that the first pretreatment compositions and/or deposited material contain less than 1 ppm of any or all of the phosphate anions or compounds listed in the preceding paragraph. The term “completely free” means that the first pretreatment compositions and/or deposited material contain less than 1 ppb of any or all of the phosphate anions or compounds listed in the preceding paragraph, if any at all.

[0068] The pH of the first pretreatment composition may be at least 1.0, such as at least 2.0, such as at least 2.2, and in some instances may be 4.0 or less, such as 3.5 or less, such

as 2.5 or less, such as 2.7 or less. The pH of the first pretreatment composition may, in some instances, be 1.0 to 4.0, such as 1.0 to 3.5, such as 2.0 to 3.0, such as 2.2 to 2.7, and may be adjusted using, for example, any acid and/or base as is necessary. The pH of the first pretreatment composition may be maintained through the inclusion of an acidic material, including water-soluble and/or water-dispersible acids, such as nitric acid, sulfuric acid, and/or phosphoric acid. The pH of the first pretreatment composition may be maintained through the inclusion of a basic material, including water-soluble and/or water-dispersible bases, such as sodium hydroxide, sodium carbonate, potassium hydroxide, ammonium hydroxide, ammonia, and/or amines such as triethylamine, methylethyl amine, or mixtures thereof.

[0069] The first pretreatment composition may comprise an aqueous medium and may optionally contain other materials such as nonionic surfactants and auxiliaries conventionally used in the art of treatment compositions. Other optional materials include surfactants that function as defoamers or substrate wetting agents. Anionic, cationic, amphoteric, and/or nonionic surfactants may be used. Defoaming surfactants may optionally be present at levels up to 1 weight percent, such as up to 0.1 percent by weight, and wetting agents are typically present at levels up to 2 percent, such as up to 0.5 percent by weight based on the total weight of the first pretreatment composition.

[0070] The first pretreatment composition may comprise a carrier, often an aqueous medium, so that the composition is in the form of a solution or dispersion of the Group IVA, Group IVB, Group IIIA, and/or Group IIIB metals in the carrier. For example, the first pretreatment composition may be an aqueous composition. The solution or dispersion may be brought into contact with the substrate by any of a variety of known techniques, such as dipping or immersion, spraying, intermittent spraying, dipping followed by spraying, spraying followed by dipping, brushing, or roll-coating. The solution or dispersion when applied to the metal substrate may be at a temperature ranging from 40° F. to 185° F., such as 60° F. to 110° F., such as 70° F. to 90° F. For example, the first pretreatment process may be carried out at ambient or room temperature. The contact time is often from 5 seconds to 15 minutes, such as 10 seconds to 10 minutes, such as 15 seconds to 3 minutes.

[0071] Following the contacting with a first pretreatment composition disclosed herein, the substrate optionally may be air dried at room temperature or may be dried with hot air, for example, by using an air knife, by flashing off the water by brief exposure of the substrate to a high temperature, such as by drying the substrate in an oven at 15° C. to 200° C. or in a heater assembly using, for example, infrared heat, such as for 10 minutes at 70° C., or by passing the substrate between squeegee rolls.

[0072] Following the contacting with a first pretreatment composition, the substrate optionally may be rinsed with tap water, deionized water, and/or an aqueous solution of rinsing agents in order to remove any residue and then optionally may be dried, for example air dried or dried with hot air as described in the preceding sentence, such as by drying the substrate in an oven at 15° C. to 100° C., such as 20° C. to 90° C., or in a heater assembly using, for example, infrared heat, such as for 10 minutes at 70° C., or by passing the substrate between squeegee rolls.

Second Pretreatment Composition

[0073] As mentioned above, the second pretreatment composition may comprise a lanthanide series metal and may be substantially free of peroxide. At least a portion of the substrate surface may be contacted with the second pretreatment composition following contacting with the first conversion composition.

[0074] The lanthanide series metal may, for example, comprise cerium, praseodymium, terbium, or combinations thereof. For example, the lanthanide series metal may be cerium. The lanthanide series metal may be present in the second pretreatment composition as a salt.

[0075] The lanthanide series metal may be present in the second pretreatment composition in an amount of at least 5 ppm based on total weight of the second pretreatment composition, such as at least 10 ppm, such as at least 20 ppm, such as at least 30 ppm, such as at least 40 ppm, such as at least 50 ppm, such as at least 400 ppm, such as at least 500 ppm, such as at least 1,000 ppm, such as at least 1,500 ppm, such as at least 2,000 ppm, and may be present in the second pretreatment composition in an amount of no more than 25,000 ppm based on total weight of the second pretreatment composition, such as no more than 10,000 ppm, such as no more than 7,000 ppm, such as no more than 6,000 ppm, such as no more than 5,000 ppm, such as no more than 3,000 ppm, such as no more than 1,000 ppm, such as no more than 500 ppm. The lanthanide series metal may be present in the second pretreatment composition an amount of 5 ppm to 25,000 ppm based on total weight of the second pretreatment composition, such as 10 ppm to 10,000 ppm, such as 20 ppm to 5,000 ppm, such as 30 ppm to 3,000 ppm, such as 40 ppm to 1,000 ppm, such as 50 ppm to 500 ppm, such as 400 ppm to 7,000 ppm, such as 500 ppm to 6,000 ppm, such as 1,000 ppm to 6,000 ppm, such as 1,500 ppm to 3,000 ppm, such as 2,000 ppm to 3,000 ppm.

[0076] The second pretreatment composition may further comprise an anion that may be suitable for forming a salt with the lanthanide series metal, such as a halogen, a nitrate, a sulfate, a phosphate, a silicate (orthosilicates and meta-silicates), carbonates, hydroxides, and the like. In examples, the halogen may exclude fluoride, since lanthanide metal fluoride complexes are generally very insoluble in water. The anion may be present in the second pretreatment composition, if at all, in an amount of at least 2 ppm based on total weight of the second pretreatment composition, such as at least 50 ppm, such as at least 150 ppm, and may be present in an amount of no more than 25,000 ppm based on total weight of the second pretreatment composition, such as no more than 18,500 ppm, such as no more than 5000 ppm. The anion may be present in the second pretreatment composition, if at all, in an amount of 2 ppm to 25,000 ppm based on total weight of the second pretreatment composition, such as 50 ppm to 18,500 ppm, such as 150 ppm to 5000 ppm.

[0077] The second pretreatment composition optionally may further comprise a Group IIIA metal. For example, the Group IIIA metal may comprise aluminum. For example, the Group IIIA metal used in the second composition may be a compound of aluminum. Suitable compounds of aluminum include, but are not limited to, aluminum chloride, aluminum nitrate, aluminum sulfate, or combinations thereof.

[0078] The Group IIIA metal may be present, if at all, in the second pretreatment composition in an amount of at least 10 ppm based on total weight of the second pretreatment

composition, such as at least 20 ppm, such as at least 25 ppm, and may be present in the second pretreatment composition in an amount of no more than 500 ppm based on total weight of the second pretreatment composition, such as no more than 100 ppm, such as no more than 75 ppm, such as no more than 50 ppm. The Group IIIA metal may be present, if at all, in the second pretreatment composition in an amount of 10 ppm to 500 ppm based on total weight of the second pretreatment composition, such as 20 ppm to 100 ppm, such as 25 ppm to 75 ppm, such as 20 ppm to 50 ppm.

[0079] The second pretreatment composition optionally may further comprise a urea. The second pretreatment composition can comprise cerium as the lanthanide series metal, aluminum and urea.

[0080] The urea may be present, if at all, in the second pretreatment composition in an amount of at least 20 ppm based on total weight of the second pretreatment composition, such as at least 40 ppm, and may be present in the second pretreatment composition in an amount of no more than 500 ppm based on total weight of the second pretreatment composition, such as no more than 100 ppm. The urea may be present, if at all, in the second pretreatment composition in an amount of 20 ppm to 500 ppm based on total weight of the second pretreatment composition, such as 40 ppm to 100 ppm.

[0081] The second pretreatment composition may be substantially free, or essentially free, or completely free, of peroxide. The second pretreatment composition can be free of peroxide.

[0082] As discussed above with respect to the first pretreatment composition, the second pretreatment composition may exclude chromium or chromium-containing compounds. That is, the second pretreatment composition and/or coatings or layers deposited from the second pretreatment composition may be substantially free, may be essentially free, and/or may be completely free of such chromium or chromium-containing compounds.

[0083] As discussed above with respect to the first pretreatment composition, the second pretreatment composition may, in some instances, exclude phosphate ions or phosphate-containing compounds and/or the formation of sludge. That is, the second pretreatment composition and/or coatings or layers deposited from the second pretreatment composition may be substantially free, or essentially free, or completely free, of phosphate ions or phosphate-containing compounds.

[0084] Optionally, the second pretreatment composition may contain no more than one lanthanide series metal cation, such that the second pretreatment composition may contain one lanthanide series metal cation and may be substantially free or essentially free or completely free of more than one lanthanide series metal cations.

[0085] The second pretreatment composition may be substantially free, essentially free, or completely free of gelatin.

[0086] The second pretreatment composition may be substantially free, essentially free, or completely free of lanthanide oxide such that the bath containing the second pretreatment composition is substantially, essentially, or completely free of lanthanide oxide.

[0087] The second pretreatment composition optionally may be substantially free, essentially free, or completely free of copper.

[0088] The pH of the second pretreatment composition may be 2.0 to 5.5, such as 2.5 to 4.5, such as 3 to 4, such as

3.5 to 5, such as 3.5 to 4.5, and may be adjusted using, for example, any acid and/or base as is necessary. The pH of the second pretreatment composition may be maintained through the inclusion of an acidic material, including water-soluble and/or water-dispersible acids, such as nitric acid, sulfuric acid, and/or organic acids, including by way of non-limiting examples, C1-C6 acids, such as formic acid, acetic acid, and/or propionic acid. The pH of the second pretreatment composition may be maintained through the inclusion of a basic material, including water-soluble and/or water-dispersible bases, such as sodium hydroxide, sodium carbonate, potassium hydroxide, ammonium hydroxide, ammonia, and/or amines such as triethylamine, methylethyl amine, or mixtures thereof.

[0089] The second pretreatment composition may comprise a carrier, often an aqueous medium, so that the composition is in the form of a solution or dispersion of the lanthanide series metal cation, such as the lanthanide series metal salt, in the carrier. For example, the second pretreatment composition may be an aqueous composition.

[0090] In examples, the solution or dispersion of the second pretreatment composition may be spontaneously applied or contacted to the substrate surface. For example, the solution or dispersion may be brought into contact with the substrate by any of a variety of known techniques, such as dipping or immersion, spraying, intermittent spraying, dipping followed by spraying, spraying followed by dipping, brushing, or roll-coating. The spontaneously applied solution or dispersion, when applied to the metal substrate, may be at a temperature ranging from 20° C. to 50° C., such as 25° C. to 40° C. For example, the spontaneously applied pretreatment process may be carried out at ambient or room temperature. The contact time is often from 15 seconds to 5 minutes, such as 30 seconds to 4 minutes, such as 1 minute to 3 minutes. As used herein, “spontaneous” or “spontaneously”, when used with respect to a pretreatment composition, refers to a pretreatment composition that is capable of reacting with and chemically altering the substrate surface and binding to it to form a protective layer in the absence of an externally applied voltage.

[0091] In other examples, the solution or dispersion of the second pretreatment composition may be electrodepositable. As used herein, an “electrodepositable pretreatment composition” refers to a composition containing a non-elemental metal, i.e., a metal-containing compound, complex, ion or the like wherein the metal is not in elemental form, that is capable of reacting with and chemically altering the substrate surface and binding to it to form a protective layer upon the introduction of an externally applied voltage. According to the present invention, electrodeposition of the second pretreatment composition may be carried out at an electrochemical potential of greater than 2.34 V, such as at least 3 V, such as at least 10 V, such as at least 15 V, and may be carried out at an electrochemical potential of no more than 300 V, such as no more than 200 V, such as no more than 100 V. Electrodeposition of the second pretreatment composition may be carried out at an electrochemical potential of greater than 2.34 V to 300 V, such as 3 V to 300 V, such as 10 V to 200 V, such as 15 V to 100 V. One skilled in the art of electrodeposition will understand the amperage requirements to achieve electrodeposition at the disclosed range of electrochemical potentials. The electrodepositable second pretreatment composition may be applied under a constantly applied power. Alternatively, the electrodeposit-

able second pretreatment composition may be applied with a pulsing power. As used herein with respect to application of the electrodepositable pretreatment composition, “pulsing” means cycling between a “current on” and a “current off” condition at a range of frequencies known to one of skill in the art of electrodeposition. For example, the second pretreatment composition may be electrodeposited by passing an electric current between an anode and the substrate that has been contacted with the first pretreatment composition, serving as a cathode, the cathode and anode being immersed in the second composition.

[0092] In examples, the electrodepositable pretreatment composition also may further comprise a resinous binder. Suitable resins include reaction products of one or more alkanolamines and an epoxy-functional material containing at least two epoxy groups, such as those disclosed in U.S. Pat. No. 5,653,823. In some cases, such resins contain beta hydroxy ester, imide, or sulfide functionality, incorporated by using dimethylolpropionic acid, phthalimide, or mercaptoglycerine as an additional reactant in the preparation of the resin. Alternatively, the reaction product is that of the diglycidyl ether of Bisphenol A (commercially available, e.g., from Shell Chemical Company as EPON 880), dimethylol propionic acid, and diethanolamine in a 0.6 to 5.0:0.05 to 5.5:1 mole ratio. Other suitable resinous binders include water-soluble and water-dispersible polyacrylic acids such as those as disclosed in U.S. Pat. Nos. 3,912,548 and 5,328,525; phenol formaldehyde resins such as those as described in U.S. Pat. No. 5,662,746; water-soluble polyamides such as those disclosed in WO 95/33869; copolymers of maleic or acrylic acid with allyl ether such as those as described in Canadian patent application 2,087,352; and water-soluble and dispersible resins including epoxy resins, aminoplasts, phenol-formaldehyde resins, tannins, and polyvinyl phenols such as those as discussed in U.S. Pat. No. 5,449,415.

[0093] In other examples, the electrodepositable pretreatment composition may be substantially free, or essentially free, or completely free, of any organic materials, such as, for example, resinous binders, gelatin, amino acids, and the like.

[0094] According to the present invention, the electrodepositable pretreatment solution or dispersion, when applied to the metal substrate, may be at a temperature ranging from 60° F. to 200° F. (15° C. to 93° C.), such as from 70° F. to 180° F. (21° C. to 82° C.), such as from 80° F. to 150° F. (27° C. to 66° C.).

[0095] Following spontaneous deposition or electrodeposition of the second pretreatment composition, the substrate optionally may be rinsed and/or dried as described above.

Cleaners

[0096] The system of the present invention optionally may further comprise a cleaner. At least a portion of the substrate surface may be cleaned prior to contacting at least a portion of the substrate surface with one of the pretreatment compositions described above in order to remove grease, dirt, and/or other extraneous matter. At least a portion of the surface of the substrate may be cleaned by physical and/or chemical means, such as mechanically abrading the surface and/or cleaning/degreasing the surface with commercially available alkaline or acidic cleaning agents that are well known to those skilled in the art. Examples of alkaline cleaners suitable for include Chemkleen™ 166HP, 166M/C,

177, 181ALP, 490MX, 2010LP, and Surface Prep 1 (SP1), Ultrax 32, Ultrax 97, Ultrax 29, and Ultrax92D, each of which are commercially available from PPG Industries, Inc. (Cleveland, OH), and any of the DFM Series, RECC 1001, and 88X1002 cleaners (commercially available from PRC-DeSoto International, Sylmar, CA), and Turco 4215-NCLT and Ridolene (commercially available from Henkel Technologies, Madison Heights, MI). Examples of acidic cleaners suitable for use include Acid Metal Cleaner (AMC) 23, AMC 239, AMC 240, and AMC 533, AMC66AW, and acetic acid. Such cleaners are often preceded and/or followed by a water rinse, such as with tap water, distilled water, or combinations thereof.

[0097] Following the cleaning step(s), the substrate optionally may be rinsed with tap water, deionized water, and/or an aqueous solution of rinsing agents in order to remove any residue. The wet substrate surface may be treated with one of the pretreatment compositions described above or the substrate may be dried prior to treating the substrate surface, such as air dried, for example, by using an air knife, by flashing off the water by brief exposure of the substrate to a high temperature, such as 15° C. to 100° C., such as 20° C. to 90° C., or in a heater assembly using, for example, infrared heat, such as for 10 minutes at 70° C., or by passing the substrate between squeegee rolls.

Film-Forming Resins

[0098] As discussed above, the present invention is directed to a system for treating a metal substrate comprising, or consisting essentially of, or consisting of, the first and second or second pretreatment compositions described above. Optionally, the system may further comprise a coating composition. The coating composition may comprise, or consist essentially of, or consist of, a film-forming resin. Any suitable technique may be used to deposit such a coating composition onto the substrate, including, for example, brushing, dipping, flow coating, spraying and the like. Optionally, however, as described in more detail below, such depositing of a coating composition may comprise an electrocoating step wherein an electrodepositable coating composition is deposited onto a metal substrate by electrodeposition. In certain other instances, as described in more detail below, such depositing of a coating composition comprises a powder coating step. In still other instances, the coating composition may be a liquid coating composition.

[0099] The coating composition may comprise a thermosetting film-forming resin or a thermoplastic film-forming resin. As used herein, the term “film-forming resin” refers to resins that can form a self-supporting continuous film on at least a horizontal surface of a substrate upon removal of any diluents or carriers present in the composition and/or upon curing at ambient or elevated temperature. Conventional film-forming resins that may be used include, without limitation, those typically used in automotive OEM coating compositions, automotive refinish coating compositions, industrial coating compositions, architectural coating compositions, coil coating compositions, and aerospace coating compositions, among others. As used herein, the term “thermosetting” refers to resins that “set” irreversibly upon curing or crosslinking, wherein the polymer chains of the polymeric components are joined together by covalent bonds. This property is usually associated with a crosslinking reaction of the composition constituents often induced, for example, by heat or radiation. Curing or cross-

linking reactions also may be carried out under ambient conditions. Once cured or crosslinked, a thermosetting resin will not melt upon the application of heat and is insoluble in solvents. As used herein, the term “thermoplastic” refers to resins that comprise polymeric components that are not joined by covalent bonds and thereby can undergo liquid flow upon heating and are soluble in solvents.

[0100] As previously indicated, the coating composition may be an electrodepositable coating composition comprising a water-dispersible, ionic salt group-containing film-forming resin that may be deposited onto the substrate by an electrocoating step wherein the electrodepositable coating composition is deposited onto the metal substrate under the influence of an applied electrical potential, i.e., by electrodeposition. The ionic salt group-containing film-forming polymer may comprise a cationic salt group containing film-forming polymer for use in a cationic electrodepositable coating composition. As used herein, the term “cationic salt group-containing film-forming polymer” refers to polymers that include at least partially neutralized cationic groups, such as sulfonium groups and ammonium groups, that impart a positive charge. The cationic salt group-containing film-forming polymer may comprise active hydrogen functional groups, including, for example, hydroxyl groups, primary or secondary amino groups, and thiol groups. Cationic salt group-containing film-forming polymers that comprise active hydrogen functional groups may be referred to as active hydrogen-containing, cationic salt group-containing film-forming polymers. Examples of polymers that are suitable for use as the cationic salt group-containing film-forming polymer include, but are not limited to, alkyd polymers, acrylics, polyepoxides, polyamides, polyurethanes, polyureas, polyethers, and polyesters, among others. The cationic salt group-containing film-forming polymer may be present in the cationic electrodepositable coating composition in an amount of 40% to 90% by weight, such as 50% to 80% by weight, such as 60% to 75% by weight based on the total weight of the resin solids of the electrodepositable coating composition. As used herein, the “resin solids” include the ionic salt group-containing film-forming polymer, curing agent (as discussed below), and any additional water-dispersible non-pigmented component(s) present in the electrodepositable coating composition.

[0101] Alternatively, the ionic salt group containing film-forming polymer may comprise an anionic salt group containing film-forming polymer for use in an anionic electrodepositable coating composition. As used herein, the term “anionic salt group containing film-forming polymer” refers to an anionic polymer comprising at least partially neutralized anionic functional groups, such as carboxylic acid and phosphoric acid groups that impart a negative charge. The anionic salt group-containing film-forming polymer may comprise active hydrogen functional groups. Anionic salt group-containing film-forming polymers that comprise active hydrogen functional groups may be referred to as active hydrogen-containing, anionic salt group-containing film-forming polymers. The anionic salt group-containing film-forming polymer may comprise base-solubilized, carboxylic acid group-containing film-forming polymers such as the reaction product or adduct of a drying oil or semi-drying fatty acid ester with a dicarboxylic acid or anhydride; and the reaction product of a fatty acid ester, unsaturated acid or anhydride and any additional unsaturated modifying materials which are further reacted with polyol. Also suit-

able are the at least partially neutralized interpolymers of hydroxy-alkyl esters of unsaturated carboxylic acids, unsaturated carboxylic acid and at least one other ethylenically unsaturated monomer. Still another suitable anionic electrodepositable resin comprises an alkyd-aminoplast vehicle, i.e., a vehicle containing an alkyd resin and an amine-aldehyde resin. Another suitable anionic electrodepositable resin composition comprises mixed esters of a resinous polyol. Other acid functional polymers may also be used such as phosphatized polyepoxide or phosphatized acrylic polymers. Exemplary phosphatized polyepoxides are disclosed in U.S. Patent Application Publication No. 2009-0045071 at [0004]-[0015] and U.S. patent application Ser. No. 13/232,093 at [0014]-[0040], the cited portions of which being incorporated herein by reference. The anionic salt group-containing film-forming polymer may be present in the anionic electrodepositable coating composition in an amount 50% to 90%, such as 55% to 80%, such as 60% to 75% based on the total weight of the resin solids of the electrodepositable coating composition.

[0102] The electrodepositable coating composition may further comprise a curing agent. The curing agent may comprise functional groups that are reactive with the functional groups, such as active hydrogen groups, of the ionic salt group-containing film-forming polymer to effectuate cure of the coating composition to form a coating. Non-limiting examples of suitable curing agents are at least partially blocked polyisocyanates, aminoplast resins and phenoplast resins, such as phenolformaldehyde condensates including allyl ether derivatives thereof. The curing agent may be present in the cationic electrodepositable coating composition in an amount of 10% to 60% by weight, such as 20% to 50% by weight, such as 25% to 40% by weight based on the total weight of the resin solids of the electrodepositable coating composition. Alternatively, the curing agent may be present in the anionic electrodepositable coating composition in an amount of 10% to 50% by weight, such as 20% to 45% by weight, such as 25% to 40% by weight based on the total weight of the resin solids of the electrodepositable coating composition.

[0103] The electrodepositable coating composition may further comprise other optional ingredients, such as a pigment composition and, if desired, various additives such as fillers, plasticizers, anti-oxidants, biocides, UV light absorbers and stabilizers, hindered amine light stabilizers, defoamers, fungicides, dispersing aids, flow control agents, surfactants, wetting agents, or combinations thereof.

[0104] The electrodepositable coating composition may comprise water and/or one or more organic solvent(s). Water can for example be present in amounts of 40% to 90% by weight, such as 50% to 75% by weight based on total weight of the electrodepositable coating composition. If used, the organic solvents may typically be present in an amount of less than 10% by weight, such as less than 5% by weight based on total weight of the electrodepositable coating composition. The electrodepositable coating composition may in particular be provided in the form of an aqueous dispersion. The total solids content of the electrodepositable coating composition may be from 1% to 50% by weight, such as 5% to 40% by weight, such as 5% to 20% by weight based on the total weight of the electrodepositable coating composition. As used herein, "total solids" refers to the

non-volatile content of the electrodepositable coating composition, i.e., materials which will not volatilize when heated to 110° C. for 15 minutes.

[0105] The cationic electrodepositable coating composition may be deposited upon an electrically conductive substrate by placing the composition in contact with an electrically conductive cathode and an electrically conductive anode, with the surface to be coated being the cathode. Alternatively, the anionic electrodepositable coating composition may be deposited upon an electrically conductive substrate by placing the composition in contact with an electrically conductive cathode and an electrically conductive anode, with the surface to be coated being the anode. An adherent film of the electrodepositable coating composition is deposited in a substantially continuous manner on the cathode or anode, respectively, when a sufficient voltage is impressed between the electrodes. The applied voltage may be varied and can be, for example, as low as one volt to as high as several thousand volts, such as between 50 and 500 volts. Current density is usually between 1.0 ampere and 15 amperes per square foot (10.8 to 161.5 amperes per square meter) and tends to decrease quickly during the electrodeposition process, indicating formation of a continuous self-insulating film.

[0106] Once the cationic or anionic electrodepositable coating composition is electrodeposited over at least a portion of the electroconductive substrate, the coated substrate may be heated to a temperature and for a time sufficient to cure the electrodeposited coating on the substrate. For cationic electrodeposition, the coated substrate may be heated to a temperature ranging from 230° F. to 450° F. (110° C. to 232.2° C.), such as from 275° F. to 400° F. (135° C. to 204.4° C.), such as from 300° F. to 360° F. (149° C. to 180° C.). For anionic electrodeposition, the coated substrate may be heated to a temperature ranging from 200° F. to 450° F. (93° C. to 232.2° C.), such as from 275° F. to 400° F. (135° C. to 204.4° C.), such as from 300° F. to 360° F. (149° C. to 180° C.), such as 200° F. to 210.2° F. (93° C. to 99° C.). The curing time may be dependent upon the curing temperature as well as other variables, for example, the film thickness of the electrodeposited coating, level and type of catalyst present in the composition and the like. For example, the curing time can range from 10 minutes to 60 minutes, such as 20 to 40 minutes. The thickness of the resultant cured electrodeposited coating may range from 10 to 50 microns.

[0107] Alternatively, as mentioned above, after the substrate has been contacted with the pretreatment compositions as described above, a powder coating composition may then be deposited onto at least a portion of the pretreated substrate surface. As used herein, "powder coating composition" refers to a coating composition in the form of a co-reactable solid in particulate form which is substantially or completely free of water and/or solvent. Accordingly, the powder coating composition disclosed herein is not synonymous to waterborne and/or solvent-borne coating compositions known in the art. The powder coating composition may comprise (a) a film forming polymer having a reactive functional group; and (b) a curing agent having a functional group that is reactive with the functional group of the film-forming polymer. Examples of powder coating compositions that may be used in the present invention include the polyester-based ENVIROCRON line of powder coating compositions (commercially available from PPG Industries,

Inc.) or epoxy-polyester hybrid powder coating compositions. Alternative examples of powder coating compositions that may be used include low temperature cure thermosetting powder coating compositions comprising (a) at least one tertiary aminourea compound, at least one tertiary aminourethane compound, or mixtures thereof, and (b) at least one film-forming epoxy-containing resin and/or at least one siloxane-containing resin (such as those described in U.S. Pat. No. 7,470,752, assigned to PPG Industries, Inc. and incorporated herein by reference); curable powder coating compositions generally comprising (a) at least one tertiary aminourea compound, at least one tertiary aminourethane compound, or mixtures thereof, and (b) at least one film-forming epoxy-containing resin and/or at least one siloxane-containing resin (such as those described in U.S. Pat. No. 7,432,333, assigned to PPG Industries, Inc. and incorporated herein by reference); and those comprising a solid particulate mixture of a reactive group-containing polymer having a T_g of at least 30° C. (such as those described in U.S. Pat. No. 6,797,387, assigned to PPG Industries, Inc. and incorporated herein by reference). The powder coating compositions are often applied by spraying, electrostatic spraying, or by the use of a fluidized bed. Other standard methods for coating application of the powder coating also can be employed such as brushing, dipping or flowing. After application of the powder coating composition, the coating is often heated to cure the deposited composition. The heating or curing operation is often carried out at a temperature in the range of from 130° C. to 220° C., such as from 170° C. to 190° C., for a period of time ranging from 10 minutes to 30 minutes, such 15 minutes to 25 minutes. The thickness of the resultant film is from 50 microns to 125 microns.

[0108] As mentioned above, after the substrate has been contacted with the pretreatment compositions as described above, a liquid coating composition may then be applied or deposited onto at least a portion of the substrate surface. As used herein, “liquid coating composition” refers to a coating composition which contains a portion of water and/or solvent that may be substantially or completely removed from the composition upon drying and/or curing. Accordingly, the liquid coating composition disclosed herein is synonymous to waterborne and/or solvent-borne coating compositions known in the art.

[0109] The liquid coating composition may comprise, for example, (a) a film forming polymer having a reactive functional group; and (b) a curing agent having a functional group that is reactive with the functional group of the film-forming polymer. In other examples, the liquid coating may contain a film forming polymer that may react with oxygen in the air or coalesce into a film with the evaporation of water and/or solvents. These film-forming mechanisms may require or be accelerated by the application of heat or some type of radiation such as Ultraviolet or Infrared. Examples of liquid coating compositions that may be used include the SPECTRACRON® line of solvent-based coating compositions, the AQUACRON® line of water-based coating compositions, and the RAYCRON® line of UV cured coatings (all commercially available from PPG Industries, Inc.). Suitable film forming polymers that may be used in the liquid coating composition may comprise a (poly) ester, an alkyd, a (poly)urethane, an isocyanurate, a (poly) urea, a (poly)epoxy, an anhydride, an acrylic, a (poly)ether, a (poly)sulfide, a (poly)amine, a (poly)amide, (poly)vinyl

chloride, (poly)olefin, (poly)vinylidene fluoride, (poly)siloxane, or combinations thereof.

[0110] The film-forming resin may, in examples, be a primer composition and/or a topcoat composition. The primer and/or topcoat compositions may be, for examples, chromate-based primers and/or advanced performance topcoats. The primer coat can be a conventional chromate-based primer coat, such as those available from PPG Industries, Inc. (product code 44GN072), or a chrome-free primer such as those available from PPG (DESOPRIME CA7502, DESOPRIME CA7521, Deft 02GN083, Deft 02GN084). Alternately, the primer coat can be a chromate-free primer coat, such as the coating compositions described in U.S. patent application Ser. No. 10/758,973, titled “CORROSION RESISTANT COATINGS CONTAINING CARBON”, and U.S. patent application Ser. Nos. 10/758,972, and 10/758,972, both titled “CORROSION RESISTANT COATINGS”, all of which are incorporated herein by reference, and other chrome-free primers that are known in the art, and which can pass the military requirement of MIL-PRF-85582 Class N or MIL-PRF-23377 Class N may also be used with the current invention.

[0111] As mentioned above, the substrate of the present invention also may comprise a topcoat. As used herein, the term “topcoat” refers to a mixture of binder(s) which can be an organic or inorganic based polymer or a blend of polymers, typically at least one pigment, can optionally contain at least one solvent or mixture of solvents, and can optionally contain at least one curing agent. A topcoat is typically the coating layer in a single or multi-layer coating system whose outer surface is exposed to the atmosphere or environment, and its inner surface is in contact with another coating layer or polymeric substrate. Examples of suitable topcoats include those conforming to MIL-PRF-85285D, such as those available from PPG (Deft 03W127A and Deft 03GY292). The topcoat may be an advanced performance topcoat, such as those available from PPG (Defthane® ELT™ 99GY001 and 99W009). However, other topcoats and advanced performance topcoats can be used as will be understood by those of skill in the art with reference to this disclosure.

[0112] The metal substrate also may comprise a self-priming topcoat, or an enhanced self-priming topcoat. The term “self-priming topcoat”, also referred to as a “direct to substrate” or “direct to metal” coating, refers to a mixture of a binder(s), which can be an organic or inorganic based polymer or blend of polymers, typically at least one pigment, can optionally contain at least one solvent or mixture of solvents, and can optionally contain at least one curing agent. The term “enhanced self-priming topcoat”, also referred to as an “enhanced direct to substrate coating” refers to a mixture of functionalized fluorinated binders, such as a fluoroethylene-alkyl vinyl ether in whole or in part with other binder(s), which can be an organic or inorganic based polymer or blend of polymers, typically at least one pigment, can optionally contain at least one solvent or mixture of solvents, and can optionally contain at least one curing agent. Examples of self-priming topcoats include those that conform to TT-P-2756A. Examples of self-priming topcoats include those available from PPG (03W169 and 03GY369), and examples of enhanced self-priming topcoats include Defthane® ELT™/ESPT and product code number 97GY121, available from PPG. However, other self-priming topcoats and enhanced self-priming topcoats can be used in

the coating system as will be understood by those of skill in the art with reference to this disclosure.

[0113] The self-priming topcoat and enhanced self-priming topcoat may be applied directly to the pretreated substrate. The self-priming topcoat and enhanced self-priming topcoat can optionally be applied to an organic or inorganic polymeric coating, such as a primer or paint film. The self-priming topcoat layer and enhanced self-priming topcoat is typically the coating layer in a single or multi-layer coating system where the outer surface of the coating is exposed to the atmosphere or environment, and the inner surface of the coating is typically in contact with the substrate or optional polymer coating or primer.

[0114] The topcoat, self-priming topcoat, and enhanced self-priming topcoat can be applied to the pretreated substrate, in either a wet or “not fully cured” condition that dries or cures over time, that is, solvent evaporates and/or there is a chemical reaction. The coatings can dry or cure either naturally or by accelerated means for example, an ultraviolet light cured system to form a film or “cured” paint.

[0115] In addition, a colorant and, if desired, various additives such as surfactants, wetting agents or catalyst can be included in the coating composition (electrodepositable, powder, or liquid). As used herein, the term “colorant” means any substance that imparts color and/or other opacity and/or other visual effect to the composition. Example colorants include pigments, dyes and tints, such as those used in the paint industry and/or listed in the Dry Color Manufacturers Association (DCMA), as well as special effect compositions. In general, the colorant can be present in the coating composition in any amount sufficient to impart the desired visual and/or color effect. The colorant may comprise from 1 to 65 weight percent, such as from 3 to 40 weight percent or 5 to 35 weight percent, with weight percent based on the total weight of the composition.

Methods

[0116] The present invention also is directed to methods for treating a metal substrate. In examples, the method of treating may comprise, or may consist essentially of, or may consist of: contacting at least a portion of a substrate surface with one of the first pretreatment compositions disclosed herein; and contacting at least a portion of the substrate surface with one of the second pretreatment compositions disclosed herein. For example, the first pretreatment composition may comprise, or consist essentially of, or consist of, a fluorometallic acid as described above and free fluoride in an amount of 10 ppm to 500 ppm based on total weight of the first pretreatment composition. For example, the second pretreatment composition may comprise, or consist essentially of, or consist of, a lanthanide series metal and may be substantially free, or essentially free, or completely free, of peroxide. The method also may further comprise contacting at least a portion of the substrate surface with a cleaner composition and/or a film-forming resin.

[0117] Treated Substrates

[0118] The present invention also may comprise a magnesium or magnesium alloy wherein:

[0119] (a) a lanthanide series metal is present in an amount of at least 500 counts as measured by X-ray fluorescence (measured using an X-Met 755, Oxford Instruments; operating parameters 60 second timed

assay, 15 Kv, 45 μ A, $L\alpha$ line, $T(p)=1.1$ μ s), such as at least 1000 counts, such as at least 2000 counts, such as at least 5000 counts;

[0120] (b) aluminum is present in an amount of at least 150 counts as measured by X-ray fluorescence (measured using an X-Met 755, Oxford Instruments; operating parameters 60 second timed assay, 15 Kv, 45 μ A, $K\alpha$ line, $T(p)=1.1$ μ s), such as at least 160 counts, such as at least 170 counts, such as at least 180 counts, such as at least 190 counts;

[0121] (c) a lanthanide series metal is present between an air/substrate interface and 1 μ m below the air/substrate interface in an amount of no more than 25 atomic % as measured by an EDX line scan collected from a surface of the substrate to the bulk of the substrate in cross-section with a 5.00 kV accelerating voltage and a 3.0 spot size, such as no more than 20 atomic %, such as no more than 15 atomic %, such as no more than 10 atomic %, such as no more than 5 atomic %, such as no more than 1 atomic %; and/or

[0122] (d) oxygen is present between the air/substrate interface and 1 m below the air/substrate interface in an amount of more than 65 atomic % as measured by an EDX line scan collected from a surface of the substrate to the bulk of the substrate in cross-section with a 5.00 kV accelerating voltage and a 3.0 spot size, such as no more than 50 atomic %, such as no more than 40 atomic %, such as no more than 30 atomic %, such as no more than 20 atomic %, such as no more than 10 atomic %.

[0123] The present invention also is directed to substrates treated with one of the systems and/or methods disclosed herein. That is, in examples, the present invention is directed to a substrate treated with a system comprising, or consisting essentially of, or consisting of: a first pretreatment composition comprising a fluorometallic acid as described above and free fluoride in an amount of 10 ppm to 500 ppm based on total weight of the first pretreatment composition and having a pH of 1.0 to 4.0; and a second pretreatment composition comprising, or consisting essentially of, or consisting of, a lanthanide series metal and being substantially free of peroxide.

[0124] In other examples, the present invention is directed to a substrate treated by a method comprising, or consisting essentially of, or consisting of: contacting at least a portion of a surface of the substrate with a first pretreatment composition comprising a fluorometallic acid as described above and free fluoride in an amount of 10 ppm to 500 ppm based on total weight of the first pretreatment composition and having a pH of 1.0 to 4.0; and contacting at least a portion of the surface with a second pretreatment composition comprising, or consisting essentially of, or consisting of, a lanthanide series metal and being substantially free of peroxide. In examples, the treated substrate may comprise a layer on at least a portion of the substrate, wherein the layer may be formed from one of the first and/or second pretreatment compositions described herein.

[0125] In examples, the treated substrate may have:

[0126] (a) a lanthanide series metal present in an amount of at least 500 counts as measured by X-ray fluorescence (measured using an X-Met 755, Oxford Instruments; operating parameters 60 second timed assay, 15 Kv, 45 μ A, $L\alpha$ line $T(p)=1.1$ μ s), such as at least 1000 counts, such as at least 2000 counts, such as at least 5000 counts;

- [0127]** (b) aluminum present in an amount of at least 150 counts as measured by X-ray fluorescence (measured using an X-Met 755, Oxford Instruments; operating parameters 60 second timed assay, 15 Kv, 45 μ A, K α line, T(p)=1.1 μ s), such as at least 160 counts, such as at least 170 counts, such as at least 180 counts, such as at least 190 counts;
- [0128]** (c) a lanthanide series metal present between an air/substrate interface and 1 m below the air/substrate interface in an amount of no more than 25 atomic % as measured by an EDX line scan collected from a surface of the substrate to the bulk of the substrate in cross-section with a 5.00 kV accelerating voltage and a 3.0 spot size, such as no more than 20 atomic %, such as no more than 15 atomic %, such as no more than 10 atomic %, such as no more than 5 atomic %, such as no more than 1 atomic % between an air/substrate interface and 1 m below the air/substrate interface in an amount of no more than 25 atomic % as measured by an EDX line scan collected from a surface of the substrate to the bulk of the substrate in cross-section with a 5.00 kV accelerating voltage and a 3.0 spot size; and/or
- [0129]** (d) oxygen present between the air/substrate interface and 1 m below the air/substrate interface in an amount of more than 65 atomic % as measured by an EDX line scan collected from a surface of the substrate to the bulk of the substrate in cross-section with a 5.00 kV accelerating voltage and a 3.0 spot size, such as no more than 50 atomic %, such as no more than 40 atomic %, such as no more than 30 atomic %, such as no more than 20 atomic %, such as no more than 10 atomic %.
- [0130]** In examples, a magnesium or magnesium alloy substrate treated with the systems or methods of the present invention may have a scribe creep on a substrate surface that is at least maintained compared to a substrate contacted with a second pretreatment composition comprising peroxide, wherein the scribe creep is measured following ASTM B117 salt spray testing for at least one week, G-85 salt spray testing for at least one week, EN3665 corrosion testing for at least 10 weeks, and/or CASS testing for at least one week.
- [0131]** Whereas specific aspects of the invention have been described in detail, it will be appreciated by those skilled in the art that various modifications and alternatives to those details could be developed in light of the overall teachings of the disclosure. Accordingly, the particular arrangements disclosed are meant to be illustrative only and not limiting as to the scope of the invention which is to be given the full breadth of the claims and aspects appended and any and all equivalents thereof.

Examples

Pretreatment Components and Process Steps

Alkaline Cleaner

[0132] In order to remove the surface oil from the metal substrates, an alkaline solution including Chemkleen 2010LP (a phosphate-free alkaline cleaner available from PPG Industries, Inc.) and Chemkleen 181ALP (a phosphate-free blended surfactant additive available from PPG Industries, Inc.) was prepared. For a 10 gallons solution, 500 mL of Chemkleen 2010LP and 50 mL of Chemkleen 181ALP were added in the DI water and the solution temperature was raised to 120° F.

Acidic Deoxidizers and First Pretreatment Compositions

[0133] The substrate surface was treated with one of the following acidic deoxidizing or first pretreatment compositions detailed below. Potassium bifluoride (99.3 weight %) was purchased from Sigma-Aldrich (St. Louis, MO), and hydrofluorosilicic acid (23 weight %) sodium hydroxide and acetic acid (99.5 weight %) were purchased from Thermofisher Acros Organics (Geel, Belgium). The pH of the composition was measured using a pH meter (DualStar pH/ISE Dual Channel Benchtop Meter, available from ThermoFisher Scientific, Waltham, Massachusetts, USA; pH probe, Fisher Scientific Accumet pH probe (Ag/AgCl reference electrode) by immersing the pH probe in the composition. Free fluoride was measured using a DualStar pH/ISE Dual Channel Benchtop Meter (ThermoFisher Scientific) equipped with a fluoride selective electrode (Orion ISE Fluoride Electrode, solid state, available from ThermoFisher Scientific) by immersing the ISE in the solution and allowing the measurement to equilibrate.

[0134] (i) PTMT I (First Pretreatment Composition)

[0135] In a clean 3-gallon plastic bucket, 11.34 liters of deionized water were added. Subsequently, hydrofluorosilicic acid (109.16 g), potassium bifluoride (6.97 g), and sodium hydroxide (9.48 g) were added in the bath. The prepared solution was heated to 80° F. and maintained under high stirring using an immersion heater (Polyscience Sous Vide Professional, Model #7306AC1B5, available from Polyscience, Niles, Illinois).

[0136] (ii) DX I (Comparative)

[0137] In a clean 3-gallon plastic bucket, 11.11 liters of deionized water were added. Subsequently, acetic acid (0.227 liter) was added in the bath and the solution was heated to 120° F. using the immersion heater described above and maintained under high stirring.

TABLE 1

Deoxidizer and First Pretreatment Compositions					
Composition	Code	Acid Component	pH	Free fluoride (ppm)	Total fluoride (ppm)
First Pretreatment	PTMT I	H ₂ SiF ₆	2.5	64	2700
Deoxidizer	DX I	CH ₃ COOH	—	—	—

Second Pretreatment Compositions

[0138] 13 pretreatment compositions each including cerium salts and optional additives were prepared. CeCl₃·7H₂O, Ce(NO₃)₃·6H₂O, and hydrogen peroxide (30 weight %) were supplied by Acros Organics (Geel, Belgium). Al(NO₃)₃·9H₂O, and Al₂(SO₄)₃, were purchased from Sigma-Aldrich (St. Louis, MO). AlCl₃·6H₂O, tungstosilicic acid, and urea (99.3 weight %) were supplied from Alfa Aesar (Ward Hill, MA).

[0139] All of the pretreatment compositions, as listed below, were prepared in DI water and maintained at room temperature. The pH of the compositions was measured using a pH meter as described above. During immersion of the substrate in the pretreatment bath, the pretreatment composition was kept under magnetic stirring or the substrate holder rack was manually agitated to maintain uniform distribution of reactive species throughout the composition.

[0140] (i) Second Pretreatment Composition 1 (PT-1)
[0141] To a clean one-gallon plastic container was added 3.78 liters of deionized water. Cerium chloride (24 g) and hydrogen peroxide (10.10 g) were then added. The composition was manually stirred using a glass rod and the composition color turned to yellow.

[0142] (ii) Second Pretreatment Composition 2 (PT-2)
[0143] To a clean one-gallon plastic container was added 3.78 liters of deionized water. Cerium chloride (5.7 g) and hydrogen peroxide (11.4 g) were then added. The composition was manually stirred using a glass rod and the composition color turned to yellow.

[0144] (iii) Second Pretreatment Composition 3 (PT-3)
[0145] To a clean one-gallon plastic container was added 3.78 liters of deionized water. Cerium chloride (51.82 g) and hydrogen peroxide (11.4 g) were then added. The composition was manually stirred using a glass rod and the composition color turned to yellow.

[0146] (iv) Second Pretreatment Composition 4 (PT-4)
[0147] To a clean one-gallon plastic container was added 3.78 liters of deionized water. Cerium chloride (24 g) was then added. The composition was manually stirred using a glass rod to dissolve the added salt.

[0148] (v) Second Pretreatment Composition 5 (PT-5)
[0149] To a clean one-gallon plastic container was added 3.78 liters of deionized water. Cerium chloride (5.7 g) was then added. The composition was manually stirred using a glass rod to dissolve the added salt.

[0150] (vi) Second Pretreatment Composition 6 (PT-6)
[0151] To a clean one-gallon plastic container was added 3.78 liters of deionized water. Cerium chloride (51.82 g) was then added. The composition was manually stirred using a glass rod to dissolve the added salt.

[0152] (vii) Second Pretreatment Composition 7 (PT-7)
[0153] To a clean one-gallon plastic container was added 3.78 liters of deionized water. Cerium nitrate (27.35 g) was then added. The composition was manually stirred using a glass rod to dissolve the added salt.

[0154] (viii) Second Pretreatment Composition 8 (PT-8)
[0155] To a clean one-gallon plastic container was added 3.78 liters of deionized water. Cerium chloride (24 g) and aluminum chloride (0.91 g) were then added. The composition was manually stirred using a glass rod to dissolve the added salts.

[0156] (ix) Second Pretreatment Composition 9 (PT-9)
[0157] To a clean one-gallon plastic container was added 3.78 liters of deionized water. Cerium chloride (24 g) and aluminum nitrate (1.42 g) were then added. The composition was manually stirred using a glass rod to dissolve the added salts.

[0158] (x) Second Pretreatment Composition 10 (PT-10)
[0159] To a clean one-gallon plastic container was added 3.78 liters of deionized water. Cerium chloride (24 g) and aluminum sulfate (1.29 g) were then added. The composition was manually stirred using a glass rod to dissolve the added salts.

[0160] (xi) Second Pretreatment Composition 11 (PT-11)
[0161] To a clean one-gallon plastic container was added 3.78 liters of deionized water. Cerium chloride (24 g), aluminum chloride (0.91 g), and urea (0.23 g) were then added. The composition was manually stirred using a glass rod to dissolve the added salts.

[0162] (xii) Second Pretreatment Composition 12 (PT-12)
[0163] To a clean one-gallon plastic container was added 3.78 liters of deionized water. Cerium chloride (24 g), aluminum nitrate (1.42 g), and urea (0.23 g) were then added. The composition was manually stirred using a glass rod to dissolve the added salts.

[0164] (xiii) Second Pretreatment Composition 13 (PT-13)
[0165] To a clean one-gallon plastic container was added 3.78 liters of deionized water. Cerium chloride (24 g), aluminum sulfate (1.29 g), and urea (0.23 g) were then added. The composition was manually stirred using a glass rod to dissolve the added salts.

TABLE 2

Second Pretreatment Compositions				
Second Pretreatment Composition	Ce (ppm)	Al (ppm)	Urea (ppm)	pH
PT-1	2788	—	—	3.21
PT-2	567	—	—	*
PT-3	5155	—	—	*
PT-4	2788	—	—	4.77
PT-5	567	—	—	*
PT-6	5155	—	—	*
PT-7	2334	—	—	*
PT-8	2788	27	—	3.94
PT-9	2788	27	—	3.99
PT-10	2788	27	—	4.18
PT-11	2788	27	61	4.12
PT-12	2788	27	61	4.09
PT-13	2788	27	61	4.26

* Not measured

[0166] E-form plus magnesium substrate was provided by USAMP from POSCO (Pohang, SK). E-form plus substrates were cut from 24" by 40" to 4" by 6" using a panel cutter prior to application of the alkaline cleaner. Cut samples were treated one of Processes A-D listed in Table 3.

[0167] Panels treated in Examples 1-6 were treated according to either process A or process C (outlined in Table 3). Panels were spray cleaned and degreased for 120 seconds at 10-15 psi in the alkaline cleaner (120° F.) using Vee-jet nozzles and rinsed with deionized water by immersing in a deionized water bath (75° F.) for 30 seconds followed by a deionized water spray rinse using a Melnor Rear-Trigger 7-Pattern nozzle set to shower mode (available from Home Depot). (For Process A) Cleaned substrates were immersed in the first pretreatment solution PTMT-1 at 80° F. or deoxidizer solution DX-1 at 120° F. for 120 seconds under high agitation, rinsed by DI water spray rinse using a Melnor Rear-Trigger 7-Pattern nozzle set to shower mode for 30 seconds. Subsequently, panels were immersed in one of PT-1 to PT-13 baths for 120 seconds at room temperature. During the immersion, a low agitation was maintained in the solution via manually shaking the panel holders. Pretreated substrates were rinsed by a deionized water spray using a Melnor Rear-Trigger 7-Pattern nozzle set to shower mode (75° F.) for 30 seconds and dried with hot air for approximately 120 seconds using a Hi-Velocity handheld blow-dryer made by Oster® (model number 078302-300-000) on high-setting.

[0168] Panels treated in Examples 7-8 were treated according to either process B or process D (Table 3). Panels were degreased and water cleaned through immersion and spraying steps as described in Examples 1-6 and Table 3. After the chemical cleaning, panels were optionally

immersed in the first pretreatment PTMT-ibath for 120 seconds (80° F.), followed by a deionized water spray rinse using the Melnor Rear-Trigger 7-Pattern nozzle set to shower mode (75° F.) for 30 seconds. These panels were immersed in one of PT-1, PT-4, and PT-7 baths where panels were controlled at a negative potential of 20 V for 30 seconds using a rectifier (Xantrax Model XFR600-2, Elkhart, Indiana, or Sorensen XG 300-5.6, Ametec, Berwyn, Pennsylvania). On each side of the panel, a stainless steel plate (9.5"×2") was submerged in the solution and connected to the positive part of the electrical circuit (in series) for counter electrochemical reactions. A low agitation was maintained in the solution by a magnetic stirrer set to -200 rpm and the bath was controlled at room temperature by immersing a cooling coil running with circulating water as coolant. Pretreated panels were rinsed by a deionized water spray using a Melnor Rear-Trigger 7-Pattern nozzle set to shower mode (75° F.) for 30 seconds and dried with hot air for approximately 120 seconds using a Hi-Velocity handheld blow-dryer made by Oster® (model number 078302-300-000) on high-setting.

TABLE 3

Description of Processes A-D	
Process A:	
Step 1	Alkaline cleaner (120 seconds, 120° F., spray application)
Step 2	Deionized water rinse (30 seconds, 75° F., immersion application)
Step 3	Deionized water rinse (30 seconds, 75° F., spray application)
Step 4	Deoxidizer or First Pretreatment (120 seconds, 80° F. or 120° F., immersion application)
Step 5	Deionized water rinse (30 seconds, 75° F., spray application)
Step 6	Second Pretreatment (120 seconds, Room Temperature, immersion application)
Step 7	Deionized water rinse (30 seconds, 75° F., spray application)
Step 8	Hot Air Dry (120 seconds, 140° F.)
Process B:	
Step 1	Alkaline cleaner (120 seconds, 120° F., spray application)
Step 2	Deionized water rinse (30 seconds, 75° F., immersion application)
Step 3	Deionized water rinse (30 seconds, 75° F., spray application)
Step 4	Deoxidizer or First Pretreatment (120 seconds, 80° F. or 120° F., immersion application)
Step 5	Deionized water rinse (30 seconds, 75° F., spray application)
Step 6	Second Pretreatment (30 seconds, -20 V, Room Temperature, immersion application)
Step 7	Deionized water rinse (30 seconds, 75° F., spray application)
Step 8	Hot Air Dry (120 seconds, 140° F.)
Process C:	
Step 1	Alkaline cleaner (120 seconds, 120° F., spray application)
Step 2	Deionized water rinse (30 seconds, 75° F., immersion application)
Step 3	Deionized water rinse (30 seconds, 75° F., spray application)
Step 4	Second Pretreatment (120 seconds, Room Temperature, immersion application)
Step 5	Deionized water rinse (30 seconds, 75° F., spray application)
Step 6	Hot Air Dry (120 seconds, 140° F.)
Process D:	
Step 1	Alkaline cleaner (120 seconds, 120° F., spray application)
Step 2	Deionized water rinse (30 seconds, 75° F., immersion application)
Step 3	Deionized water rinse (30 seconds, 75° F., spray application)
Step 4	Second Pretreatment (30 seconds, -20 V, Room Temperature, immersion application)
Step 5	Deionized water rinse (30 seconds, 75° F., spray application)
Step 6	Hot Air Dry (120 seconds, 140° F.)

[0169] After the E-form plus panels were treated according to one of Processes A-D, some of the panels were electrocoated with EPIC 200 FRAP (a cationic electrocoat with components commercially available from PPG), as detailed below. After the mixing of all the necessary components to prepare the electrocoat bath (resin, paste, and DI water), ultrafiltration was performed where ~25% of the electrocoat bath was removed, which was replenished with fresh deionized water. During the electrocoating step, panels were held ~210 V at 94° F. with a ramp time of 30 seconds, targeting the final thickness of electrocoat ~0.75±0.1 mils. Electrocoated panels were water rinsed using a spray gun set to shower mode (75° F.) for 30 seconds and then panels were baked in an oven (Despatch Model LFD-1-42) at 177° C. for 25 minutes.

[0170] Electrocoated panels were X-scribed on one side of the panel. For corrosion performance evaluation, panels were placed in GM cyclic corrosion test GMW14872 for a minimum of 14 cycles, ASTM B117 salt spray for a minimum of 7 days up to 44 days, G-85 test for a minimum of 7 cycles, EN3665 test for approximately 70 cycles, or CASS test (Copper Accelerated Acetic Acid Salt Spray test) for a minimum of 7 days. After the exposure, corroded panels were dried at ambient environment. The loose coating around the X-scribe was removed by applying a scotch filament tape (3M Industries Adhesives and Tapes Divisions, St. Paul, MN) and pulling it off. Afterwards, the width of exposed metal region along the scribe was recorded for 10 locations and averaged to assess the corrosion performance of the panel. In cases where scribe creep was too wide or the coating came off the panel while tape pulling, the scribe width was reported as 25 mm (i.e., FAIL) and indicates catastrophic delamination of the electrocoat layer that precluded reliable scribe creep measurements. As used herein, scribe creep refers to the area of paint loss around the scribe either through corrosion or disbondment (e.g., affected paint to affected paint). One skilled in the art understands that there is an inherent variability between conditions of different corrosion tests and that therefore corrosion performance of treated panels may vary from one standardized corrosion test to another (e.g., from GM cyclic corrosion testing GMW14872 to ASTM B117 salt spray testing).

[0171] In Example 5, as described in more detail below, panels also were exposed to dry and wet adhesion testing in order to assess the adhesion performance.

[0172] As described below, some panels were analyzed for deposition of cerium or aluminum using X-ray fluorescence (measured using X-Met 7500, Oxford Instruments; operating parameters for cerium: 60 second timed assay, 15 Kv, 45 µA, La, T(p)=1.1 µs; operating parameters for aluminum: 60 second timed assay, 15 Kv, 45 µA, Kα, T(p)=1.1 µs).

[0173] As described below some panels were evaluated using cross-sectional FE-SEM and EDX analysis. Substrate sections were mounted in epoxy overnight. After curing, the mounts were ground and polished using an abrasive pad followed by an additional 6-minute polishing cycle with 0.5 µm media at the end of the process. The samples were then placed on aluminum stubs with carbon tape, coated with Au/Pd for 20 seconds, and analyzed in the Quanta 250 FEG SEM under high vacuum. EDX line scans were collected from the surface of each substrate to the bulk of the substrates in cross-section with a 5.00 kV accelerating voltage and a 3.0 spot size.

Example 1

Corrosion Performance on E-Form Plus Panels
Treated with Alkaline Cleaner, First Pretreatment
PTMT I, and Second Pretreatments PT-1, PT-4, or
PT-7 (Process A)

[0174] Fifteen (15) E-form plus panels were treated according to Process A (using PTMT I) (Table 3), with five panels being treated with PT-1, five panels being treated with PT-4, and five panels being treated with PT-7. For each pretreatment, one panel (without electrocoating) was evaluated for cerium deposition using XRF, SEM imaging (PT-1 and PT-4 only), and EDS line scans (PT-1 and PT-4 only) as described above. Data are reported in FIGS. 1A, 1C to 1F. For each pretreatment, four of the panels were then electrocoated with EPIC 200 FRAP as described above and two panels were exposed to GMW14872 corrosion testing (50 cycles) and two panels were exposed to B117 continuous salt spray corrosion testing (44 days). Corrosion performance data are reported in FIG. 1B.

[0175] The data in Example 1 demonstrate that, when hydrogen peroxide was eliminated, i.e., pretreatment compositions PT-4 and PT-7, cerium was still deposited on magnesium substrate (FIG. 1A) and corrosion performance was maintained (FIG. 1B). The data also demonstrate that a cerium oxide layer was deposited on the magnesium alloy surface. The oxide layer was thinner on the panel treated PT-4 (which excluded hydrogen peroxide) than was the oxide layer formed on the panel treated with PT-1 (which included hydrogen peroxide). Notably, panels treated with PT-4 demonstrated corrosion performance that was comparable to panels treated with PT-1.

Example 2

Corrosion Performance on E-Form Plus Panels
Treated with Alkaline Cleaner, First Pretreatment
PTMT I, and Pretreatments PT-1 to PT-6 (Process
A)

[0176] Forty-nine (49) E-form plus panels were treated according to Process A (using PTMT I) (Table 3), with seven panels being treated with one of PTMT I only and seven panels being treated with one of PT-1 to PT-6. For PTMT I only treatment and for each pretreatment, one panel (without electrocoating) was evaluated for cerium deposition using XRF as described above. Data are reported in FIG. 2A. For each treatment, six of the panels were then electrocoated with EPIC 200 FRAP as described above. Two of these panels were exposed to CASS corrosion testing (10 days), two were exposed to B117 continuous salt spray corrosion testing (24 days), and two were exposed to G-85 cyclic corrosion testing (14 cycles). Corrosion performance data are reported in FIG. 2B.

[0177] Data are reported in FIG. 2. The data in Example 2 demonstrate that, when hydrogen peroxide was eliminated from the pretreatment composition, cerium was still deposited on magnesium substrate (FIG. 2A) and corrosion performance was improved with lower levels of cerium (PT-2 vs. PT-4) in the pretreatment bath compared to higher levels of cerium and remained comparable on panels treated with pretreatment compositions having higher levels of cerium (PT-1 to PT-4 and PT-3 to PT-6) (FIG. 2B).

Example 3

Corrosion Performance on E-Form Plus Panels
Treated with Alkaline Cleaner, and Second
Pretreatments PT-1 to PT-3 (Process C)

[0178] Twenty-one (21) E-form plus panels were treated according to Process C (Table 3), with seven panels being treated with PT-1, seven panels being treated with PT-2, and seven panels being treated with PT-3. For each pretreatment, one panel (without electrocoating) was evaluated for cerium deposition using XRF, SEM imaging (PT-1 only), and EDS line scans (PT-1 only) as described above. Data are reported in FIG. 3A. For each pretreatment, six of the panels were then electrocoated with EPIC 200 FRAP as described above and two of those panels were exposed to CASS corrosion testing (10 days), two were exposed to B117 continuous salt spray corrosion testing (24 days), and two were exposed to G-85 corrosion testing (14 cycles). Corrosion performance data are reported in FIG. 3B.

[0179] The data from Example 3 demonstrate that even when hydrogen peroxide was present in the pretreatment bath, treatment of the substrate with a PTMT I was needed for corrosion performance. Although cerium was deposited on the substrate surface (FIG. 3A), corrosion performance was poor (FIG. 3B), suggesting that treatment with a PTMT I pretreatment composition was important in achieving corrosion performance (FIG. 2B).

Example 4

Corrosion Performance on E-Form Plus Panels
Treated with Alkaline Cleaner, First Pretreatment
PTMT I, and Second Pretreatments PT-4 with
Different Immersion Times (Process A)

[0180] Twenty-one (21) E-form plus panels were treated according to Process A (using PTMT I) (Table 3), with seven panels being immersed in PT-4 for 2 minutes, seven panels being immersed in PT-4 for 5 minutes, and seven panels being immersed in PT-4 for 10 minutes. For each immersion time, one panel (without electrocoating) was evaluated for cerium deposition using XRF as described above. Data are reported in FIG. 4A. For each immersion time, six of the panels were then electrocoated with EPIC 200 FRAP as described above and two of those panels were exposed to CASS corrosion testing (10 days), two were exposed to B117 continuous salt spray corrosion testing (25 days), and two were exposed to G-85 corrosion testing (14 cycles). Corrosion performance data are reported in FIG. 4B.

[0181] The data in Example 4 demonstrate that immersion of magnesium alloy substrate in a pretreatment bath without hydrogen peroxide for more than 2 minutes impaired corrosion performance (FIG. 4B) even though higher deposition of cerium was achieved (FIG. 4A). The panels immersed in PT-4 for more than 2 minutes had a powdery appearance on the substrate surface.

Example 5

Corrosion Performance on E-Form Plus Panels
Treated with Alkaline Cleaner, First Pretreatment
PTMT I, and Second Pretreatments PT-8 to PT-13
(Process A)

[0182] Forty-nine (49) E-form plus panels were treated according to Process A (using PTMT I) (Table 3), with seven

panels being treated with one of PT-1, PT-8, PT-9, PT-10, PT-11, PT-12, or PT-13. For each pretreatment, one panel (without electrocoating) was evaluated for cerium and aluminum deposition using XRF as described above. Data are reported in FIG. 5A. For each pretreatment, six of the panels were then electrocoated with EPIC 200 FRAP as described above and two of those panels were exposed to CASS corrosion testing (10 days). Corrosion performance data are reported in FIG. 5B.

[0183] White topcoat was also applied to twenty-eight of the electrocoated panels (not exposed to corrosion testing). The topcoat is available from PPG Industries, Inc. as a three-part system composed of a primer, basecoat, and clearcoat. The product codes, dry film thickness ranges, and bake conditions are shown in Table 4 below.

TABLE 4			
Three Part Topcoat System			
Layer	Product Code	Dry Film Thickness Range (mils)	Bake (Temperature/Time)
Primer	SCP6534	0.95 ± 0.15	141° C./30 minutes
Basecoat	UDCT6466	1.1 ± 0.1	None
Clearcoat	TMAC9000	1.9 ± 0.1	82° C./7 minutes then 141° C./30 minutes

[0184] The paint adhesion for panels treated with each pretreatment composition was then tested under dry (unexposed) and wet (exposed) conditions. For each pretreatment composition tested, two panels were tested in unexposed conditions and two panels were treated in exposed conditions.

[0185] For the dry adhesion test, a razor blade was used to scribe eleven lines parallel and perpendicular to the length of the one of the electrocoated panels. The resultant grid area of the scribed lines was 0.5"×0.5" to 0.75" to 0.75" square. Dry adhesion was assessed by using 3M's Fiber 898 tape, which was firmly adhered over the scribed grid area by finger rubbing it multiple times prior to pulling it off. The crosshatch area was evaluated for paint loss on a scale from 0 to 10, with 0 being total paint loss and 10 being absolutely no paint loss (Table 5). An adhesion value of 8 is considered acceptable in the automotive industry.

[0186] For the exposed adhesion test, following topcoat application, the panel was immersed in deionized water (40° C.) for ten days, at which time the panels were removed, wiped with a towel to dry and allowed to sit at ambient temperature for forty-five minutes prior to crosshatching and tape-pulling to evaluate paint adhesion as described above.

[0187] The rating scale used in Example 5 for adhesion testing is shown in Table 5 and is defined by a high rating indicative of greater adhesion between the substrate surface, pretreatment film, and the organic coating layer (e.g.: electrocoat, topcoat, or powdercoat). Exemplary images corresponding to each of the ratings of 1 to 10 are shown in FIG. 5D. Adhesion performance data are shown in FIG. 5C.

TABLE 5	
Crosshatch Rating Description	
Rating	Percent Paint Loss
10	Perfect Paint Adhesion (0% Paint Loss)
9	5% Paint Loss

TABLE 5-continued	
Crosshatch Rating Description	
Rating	Percent Paint Loss
8	10% Paint Loss
7	25% Paint Loss
6	50% Paint Loss
5	60% Paint Loss
4	70% Paint Loss
3	80% Paint Loss
2	90% Paint Loss
1	Greater than 95% Paint Loss
0	100% Paint Loss

[0188] As shown in FIG. 5A, aluminum deposition increased when aluminum salts were included in the pretreatment composition. PT-8 to PT-13 did not include hydrogen peroxide, and the cerium counts were lower on panels treated with these pretreatments compared to panels treated with PT-1, which included hydrogen peroxide (FIG. 5A). Notably, corrosion performance of panels treated in Example 5 were comparable across pretreatment compositions PT-8 to PT-13 and PT-1 (comparative). As shown in FIG. 5C, the data from Example 5 demonstrate improved adhesion of the coatings deposited onto the substrate surface on panels treated in pretreatment baths containing urea and aluminum and without hydrogen peroxide, while also maintaining corrosion performance.

Example 6

Corrosion Performance on E-Form Plus Panels Treated with Alkaline Cleaner, Deoxidizer DX I, and Second Pretreatments PT-1, PT-4 and PT-7 (Process A)

[0189] Twenty-eight (28) E-form plus panels were treated according to Process A (using DX I) (Table 3), with seven panels being treated with one of PT-1, PT-4, or PT-7. Seven panels were treated with DX I without any additional pretreatment. For each treatment, one panel (without electrocoating) was evaluated using XRF, SEM imaging, and EDS line scans as described above. Data are reported in FIG. 6A and FIGS. 6C to 6H. For each treatment, six of the panels were electrocoated with EPIC 200 FRAP as described above and two of those panels were exposed to CASS corrosion testing (10 days), two panels were exposed to B117 continuous salt spray testing (14 days), and two panels were exposed to EN3665 corrosion testing (70 cycles). Corrosion performance data are reported in FIG. 6B.

[0190] The data from Example 6 demonstrate that when hydrogen peroxide is eliminated from the pretreatment bath, treatment of the substrate with a composition that converts the substrate surface is needed for corrosion performance because treatment with acetic acid did not provide the same corrosion performance as did treatment with PTMT I (see Example 3, FIG. 3).

Example 7

Corrosion Performance on E-Form Plus Panels Treated with Alkaline Cleaner, First Pretreatment PTMT I, and Second Pretreatments PT-1, PT-4 or PT-7 Through Process B

[0191] Fifteen (15) E-form plus panels were treated according to Process B (Table 3), with five panels being

treated with one of PT-1, PT-4, or PT-7. For each pretreatment, one panel (without electrocoating) was evaluated using XRF, SEM imaging, and EDS line scans as described above. Data are reported in FIG. 7A and FIGS. 7C to 7H. For each pretreatment, four of the panels were electrocoated with EPIC 200 FRAP as described above and two of those panels were exposed to CASS corrosion testing (10 days) and two panels were exposed to B117 continuous salt spray testing (41 days). Corrosion performance data are reported in FIG. 7B.

[0192] Data are reported in FIG. 7. The data from Example 7 demonstrate that corrosion performance in an electrolytically applied pretreatment composition is improved when hydrogen peroxide is eliminated from the bath.

Example 8

Corrosion Performance on E-Form Plus Panels Treated with Alkaline Cleaner, and Second Pretreatments PT-1, PT-4 or PT-7 Through Process D

[0193] Nine E-form plus panels were treated according to Process D (Table 4), with three panels being treated with one of PT-1, PT-4, or PT-7. For each pretreatment, one panel (without electrocoating) was evaluated using XRF, SEM imaging, and EDS line scans as described above. Data are reported in FIG. 8A and FIGS. 8C to 8H. For each pretreatment, two panels were electrocoated with EPIC 200 FRAP as described above and were exposed to CASS corrosion testing (10 days). Corrosion performance data are reported in FIG. 8B.

[0194] These data also demonstrate that when hydrogen peroxide is eliminated from the pretreatment bath, treatment of the substrate with a composition that converts the substrate surface is needed for corrosion performance.

[0195] It will be appreciated by skilled artisans that numerous modifications and variations are possible in light of the above disclosure without departing from the broad inventive concepts described and exemplified herein. Accordingly, it is therefore to be understood that the foregoing disclosure is merely illustrative of various exemplary aspects of this application and that numerous modifications and variations can be readily made by skilled artisans which are within the spirit and scope of this application and the accompanying claims.

1. A system for treating a magnesium or a magnesium alloy substrate comprising:

- a first pretreatment composition comprising a fluorometallic acid and free fluoride in an amount of 10 ppm to 500 ppm based on total weight of the first pretreatment composition and having a pH of 1.0 to 4.0; and
- a second pretreatment composition comprising a lanthanide series metal, the second pretreatment composition being substantially free, or essentially free, or completely free, of peroxide.

2. The system of claim 1, wherein the fluorometallic acid comprises a metal comprising a Group IIIA metal, a Group IVA metal, a Group IVB metal, and/or a Group VIII metal.

3. (canceled)

4. The system of claim 2, wherein the fluorometallic acid comprises the metal in an amount of 10 ppm to 2,000 ppm based on total weight of the first pretreatment composition.

5. The system of claim 1, wherein the first pretreatment composition further comprises a hydroxide source and/or a fluoride source in addition to the fluorometallic acid.

6-7. (canceled)

8. The system of claim 1, wherein the second pretreatment composition comprises the lanthanide series metal in an amount of 5 ppm to 25,000 ppm based on total weight of the second pretreatment composition.

9. The system of claim 1, wherein the second pretreatment composition further comprises a Group IIIA metal and/or a urea.

10. The system of claim 9, wherein the second pretreatment composition comprises the Group IIIA metal in an amount of 10 ppm to 500 ppm based on total weight of the second pretreatment composition and/or the urea in an amount of 20 ppm to 500 ppm based on total weight of the second pretreatment composition.

11. The system of claim 1, further comprising a cleaner composition.

12-13. (canceled)

14. The system of claim 1, further comprising a film-forming composition.

15. (canceled)

16. A method of treating a magnesium or a magnesium alloy substrate comprising:

- contacting at least a portion of a substrate surface with a first pretreatment composition comprising a fluorometallic acid and free fluoride in an amount of 10 ppm to 500 ppm based on total weight of the first pretreatment composition and having a pH of 1.0 to 4.0; and
- contacting at least a portion of the substrate surface with a second pretreatment composition comprising a lanthanide series metal and being substantially free, or essentially free, or completely free, of peroxide.

17. The method of claim 16, wherein the fluorometallic acid comprises a metal comprising a Group IIIA metal, a Group IVA metal, a Group IVB metal, and/or a Group VIII metal.

18. The method of claim 16, further comprising contacting at least a portion of the substrate surface with a cleaner composition prior to the contacting with one of the pretreatment compositions.

19. The method of claim 16, further comprising contacting at least a portion of the substrate surface with a coating composition comprising a film-forming resin following the contacting with the pretreatment compositions.

20. The method of claim 16, wherein the contacting with the second pretreatment composition comprises a spontaneous contacting.

21. The method of claim 16, wherein the contacting with the second pretreatment composition comprises passing an electric current between an anode and the substrate that has been contacted with the first pretreatment composition, serving as a cathode, said cathode and anode being immersed in the second composition.

22. (canceled)

23. A magnesium or magnesium alloy substrate treated with the system of claim 1, wherein (a) at least 500 counts of a lanthanide series metal is present as measured by X-ray fluorescence (measured using an X-Met 755, Oxford Instruments; operating parameters 60 second timed assay, 15 Kv, 45 μ A, $L\alpha$ line, $T(p)=1.1 \mu$ s); (b) at least 150 counts of aluminum as measured by X-ray fluorescence (measured using an X-Met 755, Oxford Instruments; operating param-

eters 60 second timed assay, 15 Kv, 45 μ A, K α line, T(p)=1.1 μ s); (c) no more than 25 atomic % of a lanthanide series metal between an air/substrate interface and 1 m below the air/substrate interface as measured by an EDX line scan collected from a surface of the substrate to the bulk of the substrate in cross-section with a 5.00 kV accelerating voltage and a 3.0 spot size; and/or (d) no more than 65 atomic % of oxygen between the air/substrate interface and 1 m below the air/substrate interface as measured by an EDX line scan collected from a surface of the substrate to the bulk of the substrate in cross-section with a 5.00 kV accelerating voltage and a 3.0 spot size.

- 24. (canceled)
- 25. The substrate of claim 24, comprising a first layer formed by the first pretreatment composition and/or a second layer formed by the second pretreatment.
- 26-28. (canceled)
- 29. The substrate of claim 23, wherein the substrate comprises a vehicle, a part, an article, a heat exchanger, an appliance, a personal electronic device, a multi-metal article, or combinations thereof.
- 30. The substrate of claim 29, wherein the vehicle comprises an automobile or an aircraft.
- 31. The substrate of claim 23, wherein the substrate comprises a three-dimensional component formed by an additive manufacturing process.
- 32. (canceled)

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