



US 20220145486A1

(19) **United States**

(12) **Patent Application Publication**  
**McCall et al.**

(10) **Pub. No.: US 2022/0145486 A1**

(43) **Pub. Date: May 12, 2022**

(54) **ENHANCED ANODIZATION  
FUNCTIONALITY IN AL-RARE EARTH  
ELEMENT-BASED ALLOYS**

**Related U.S. Application Data**

(60) Provisional application No. 63/112,792, filed on Nov. 12, 2020.

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**Publication Classification**

(51) **Int. Cl.**  
**C25D 11/04** (2006.01)  
**C22C 21/04** (2006.01)  
(52) **U.S. Cl.**  
CPC ..... **C25D 11/045** (2013.01); **C22C 21/04** (2013.01)

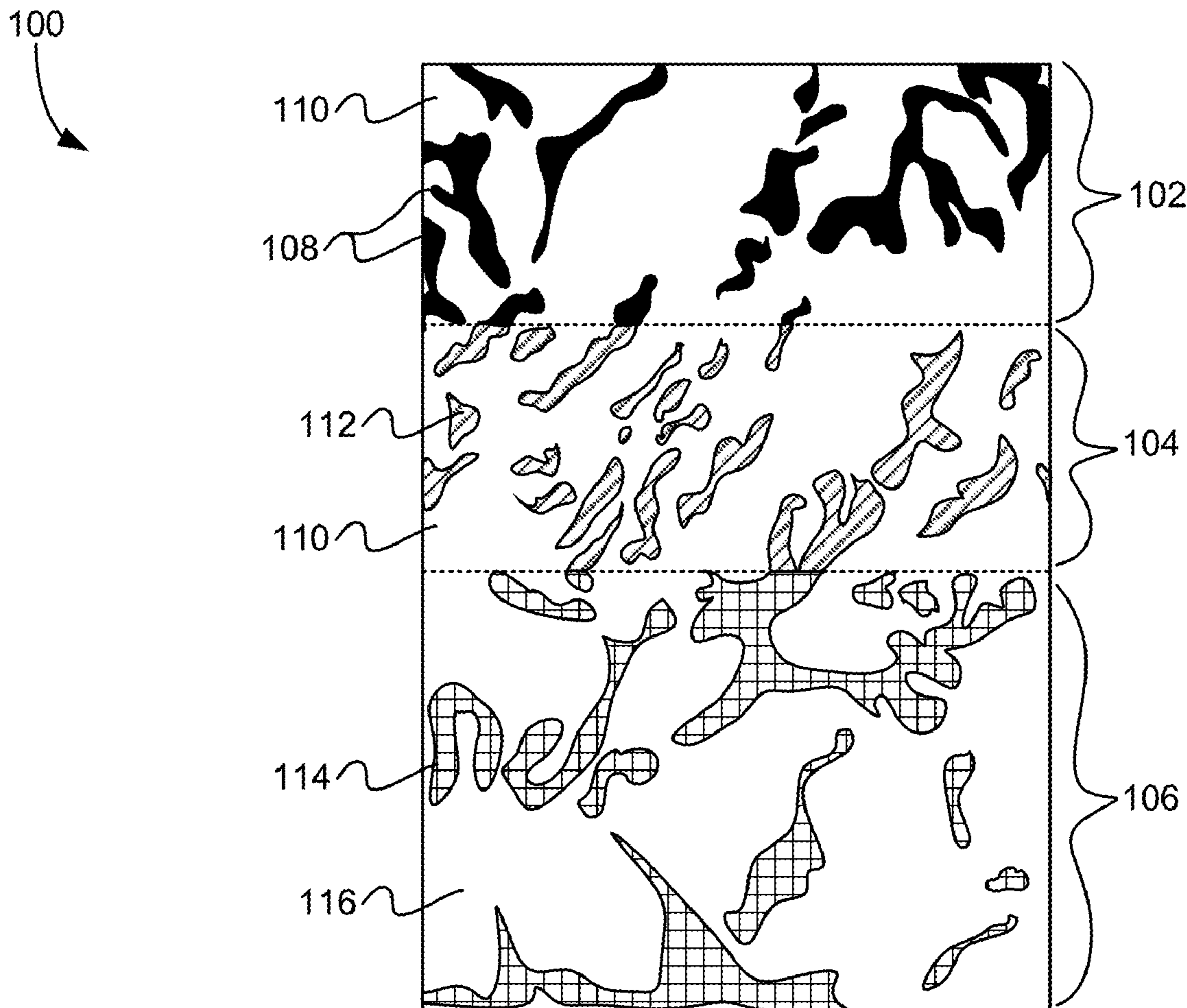
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(57) **ABSTRACT**

A product includes an aluminum alloy having an anodized layer. The alloy has a bulk composition including at least 1 wt. % of one or more rare earth elements (REEs). A product includes microstructures extending across a boundary defined between an anodized layer and an unoxidized alloy. Each microstructure includes an intermetallic phase transitioning to an oxidized intermetallic phase across the boundary. A product includes an anodized layer where up to 90% of a thickness of the layer includes voids resulting at least in part from dissolution of a rare earth element oxidized intermetallic phase. The voids are in a morphology of the dissolved oxidized intermetallic phase.

(21) Appl. No.: **17/522,745**

(22) Filed: **Nov. 9, 2021**



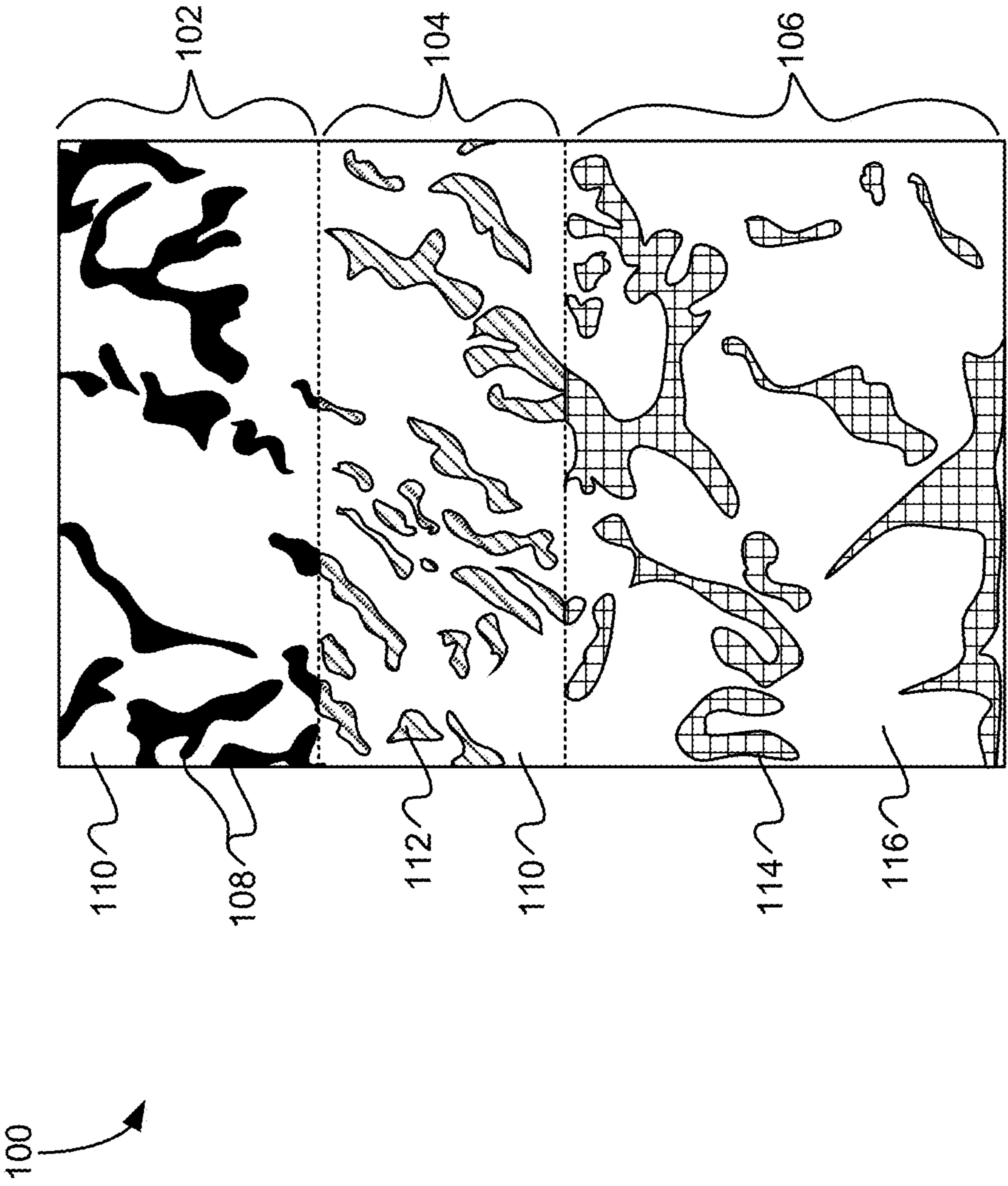


FIG. 1

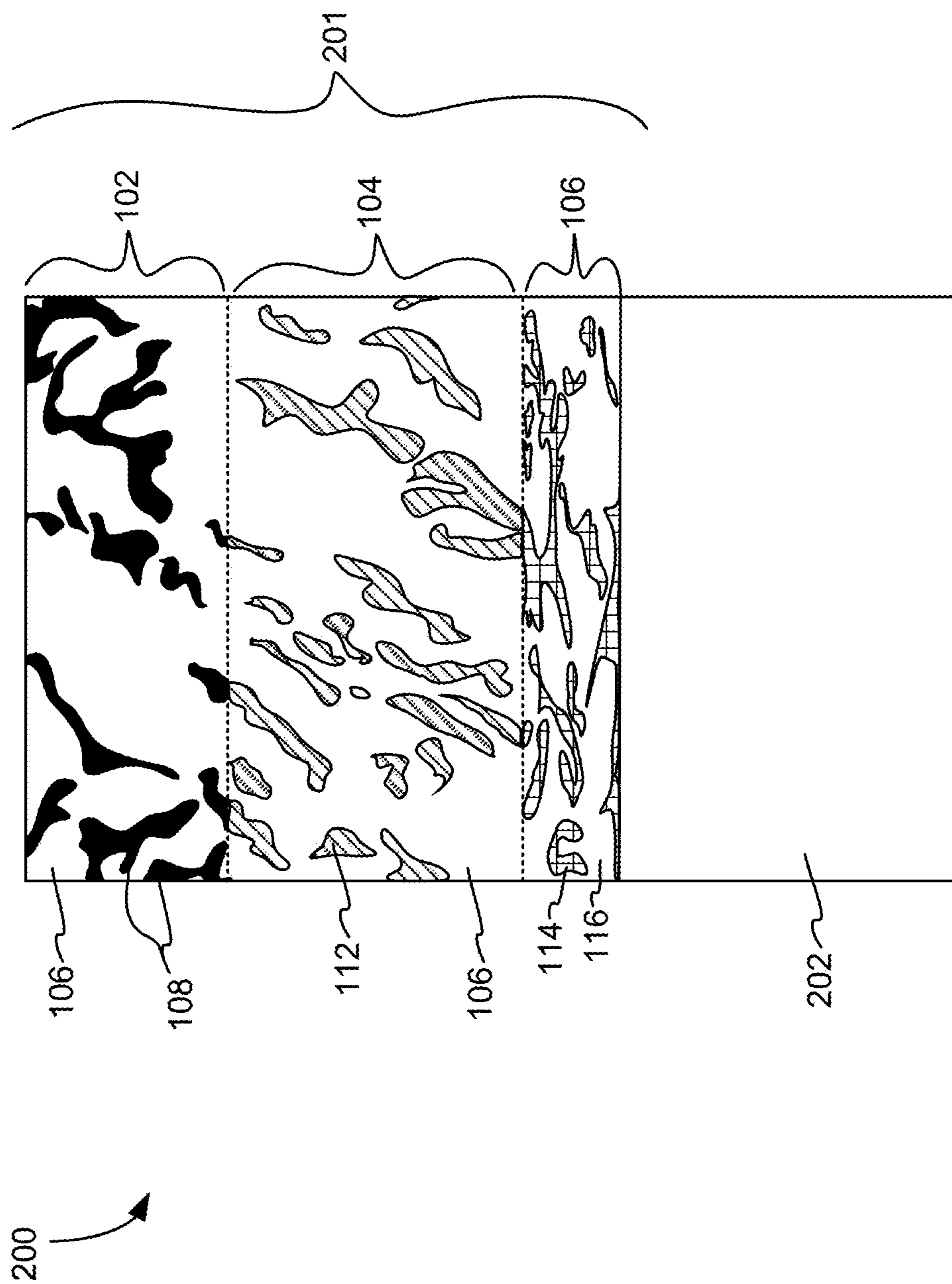


FIG. 2

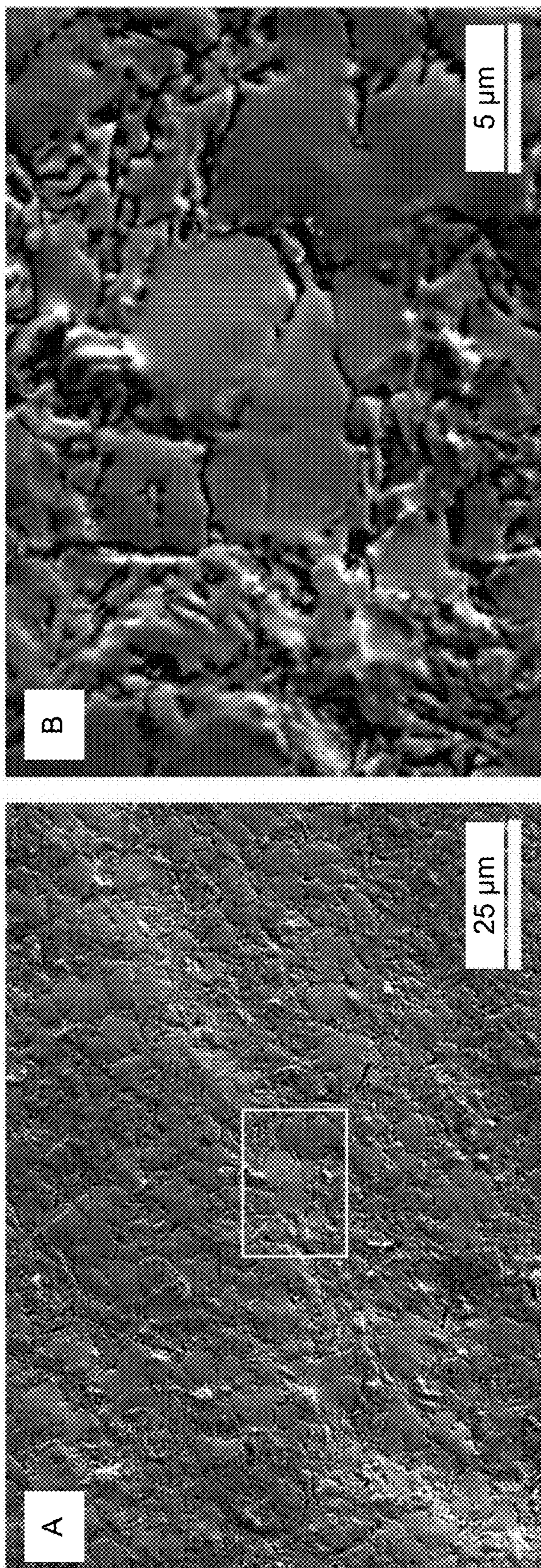


FIG. 3

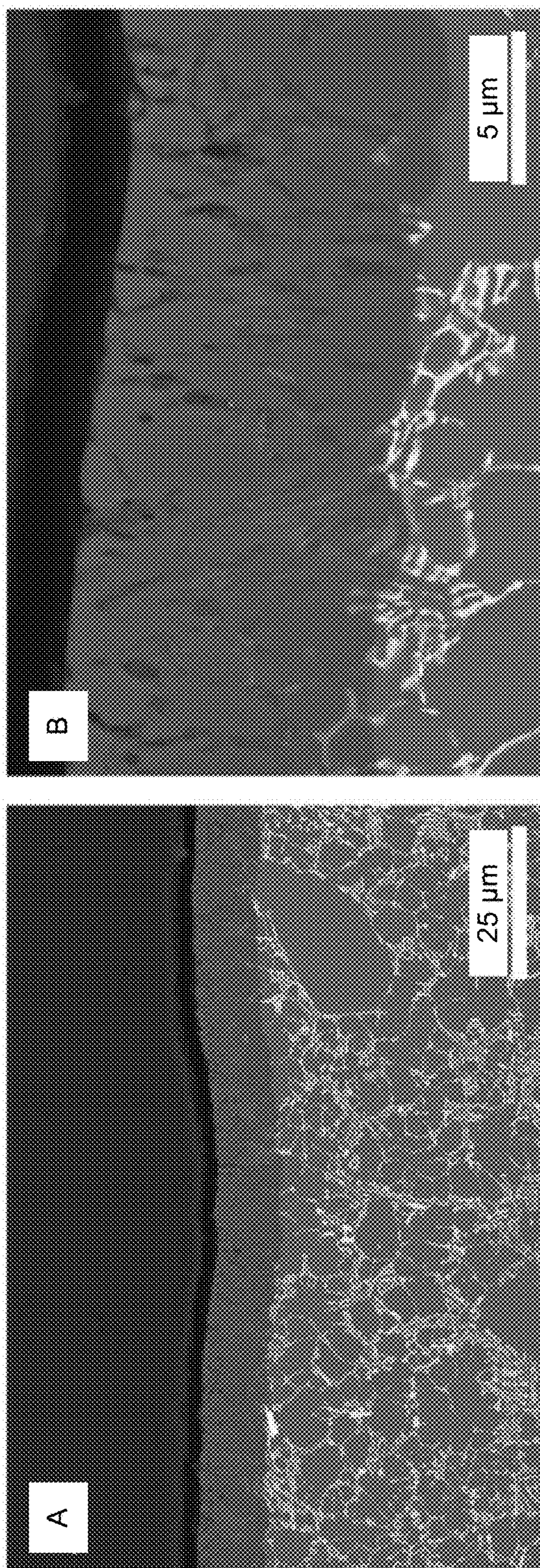


FIG. 4

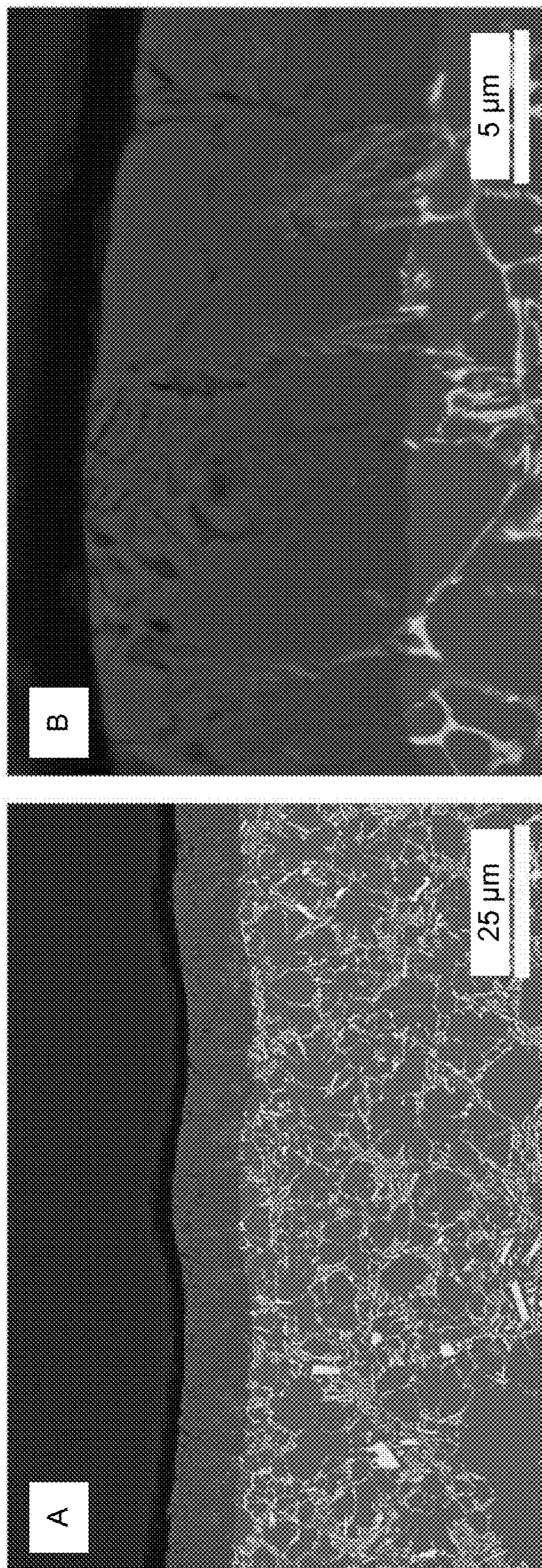


FIG. 5

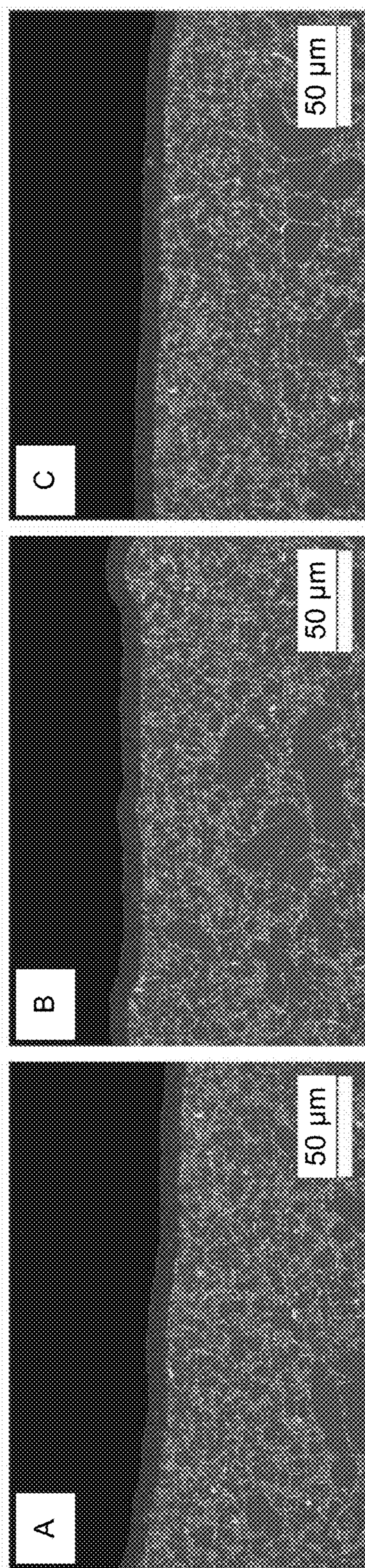


FIG. 6

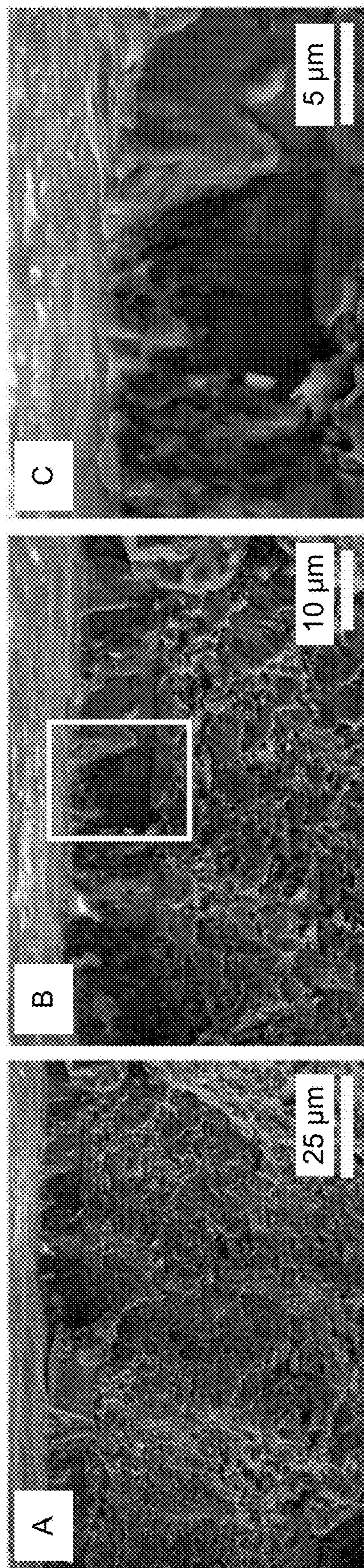


FIG. 7





FIG. 8

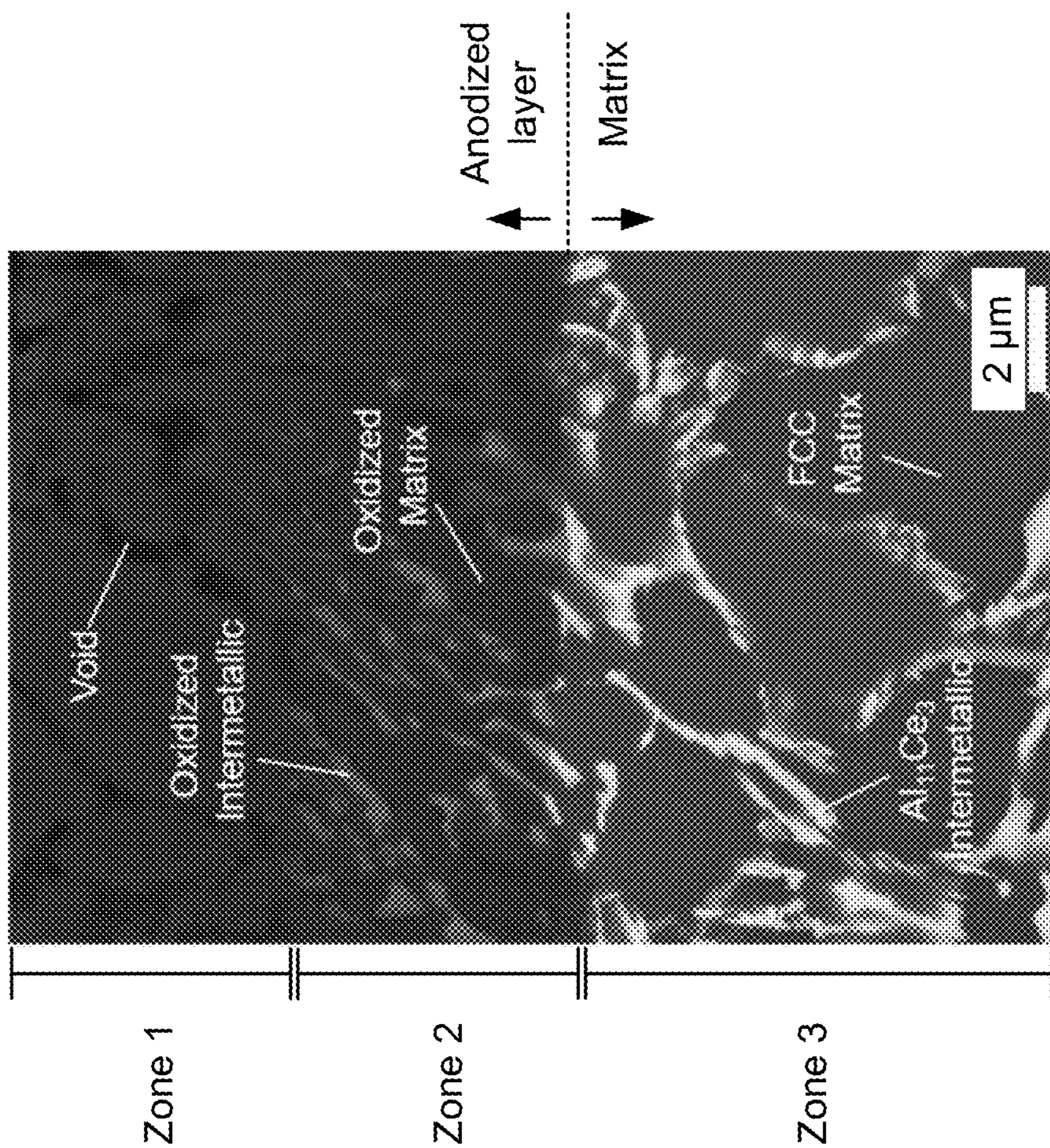


FIG. 9

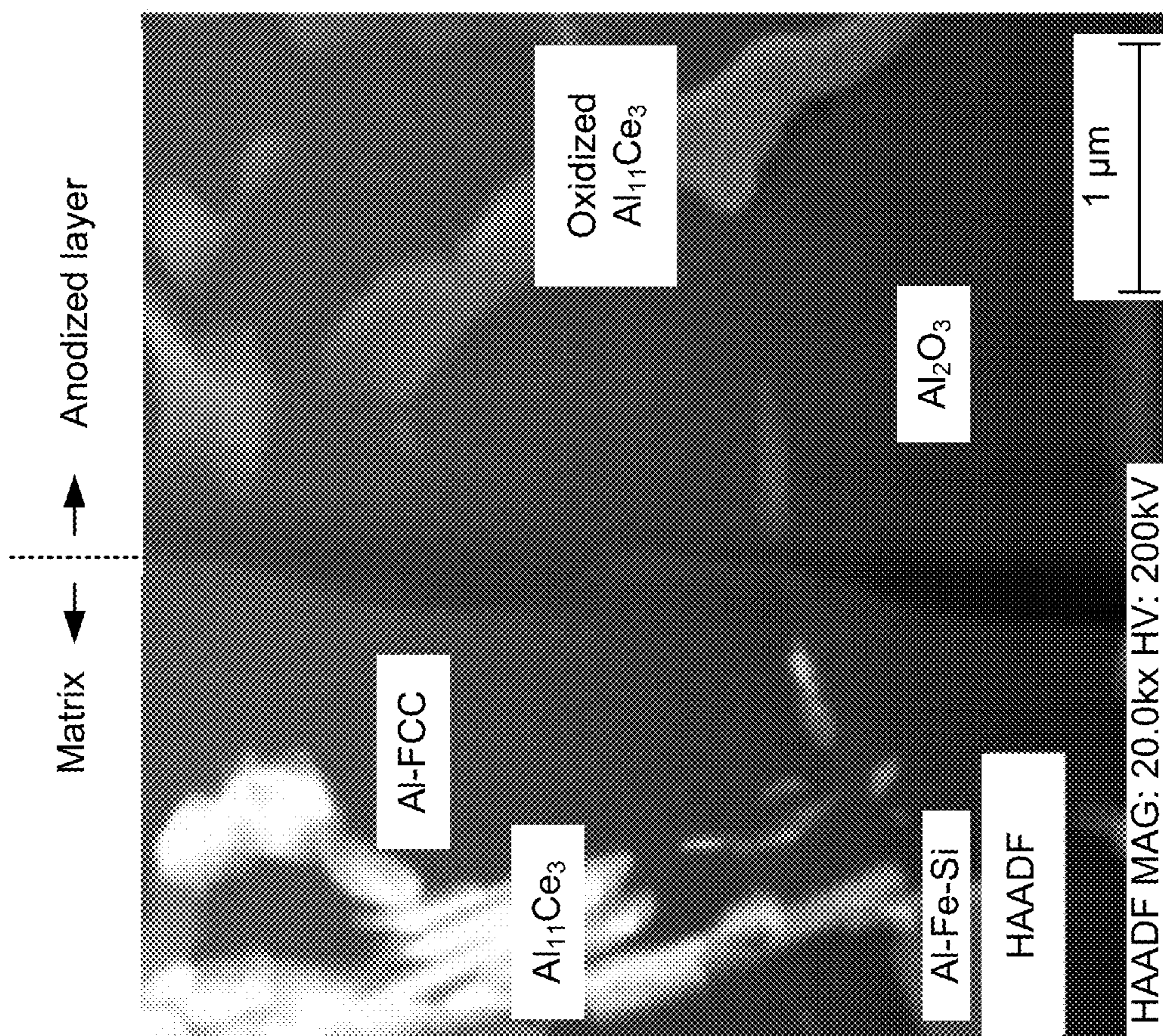


FIG. 10

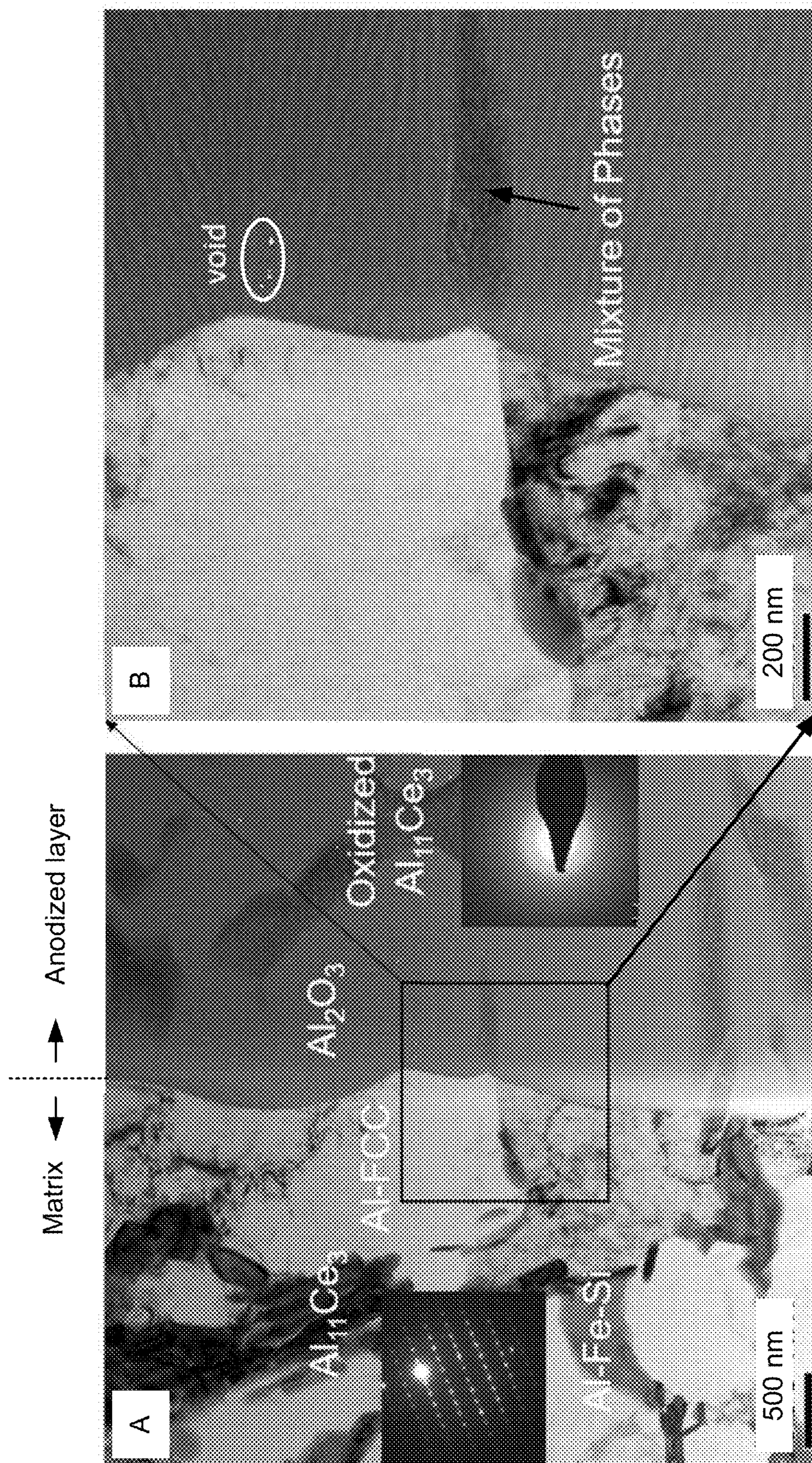


FIG. 11

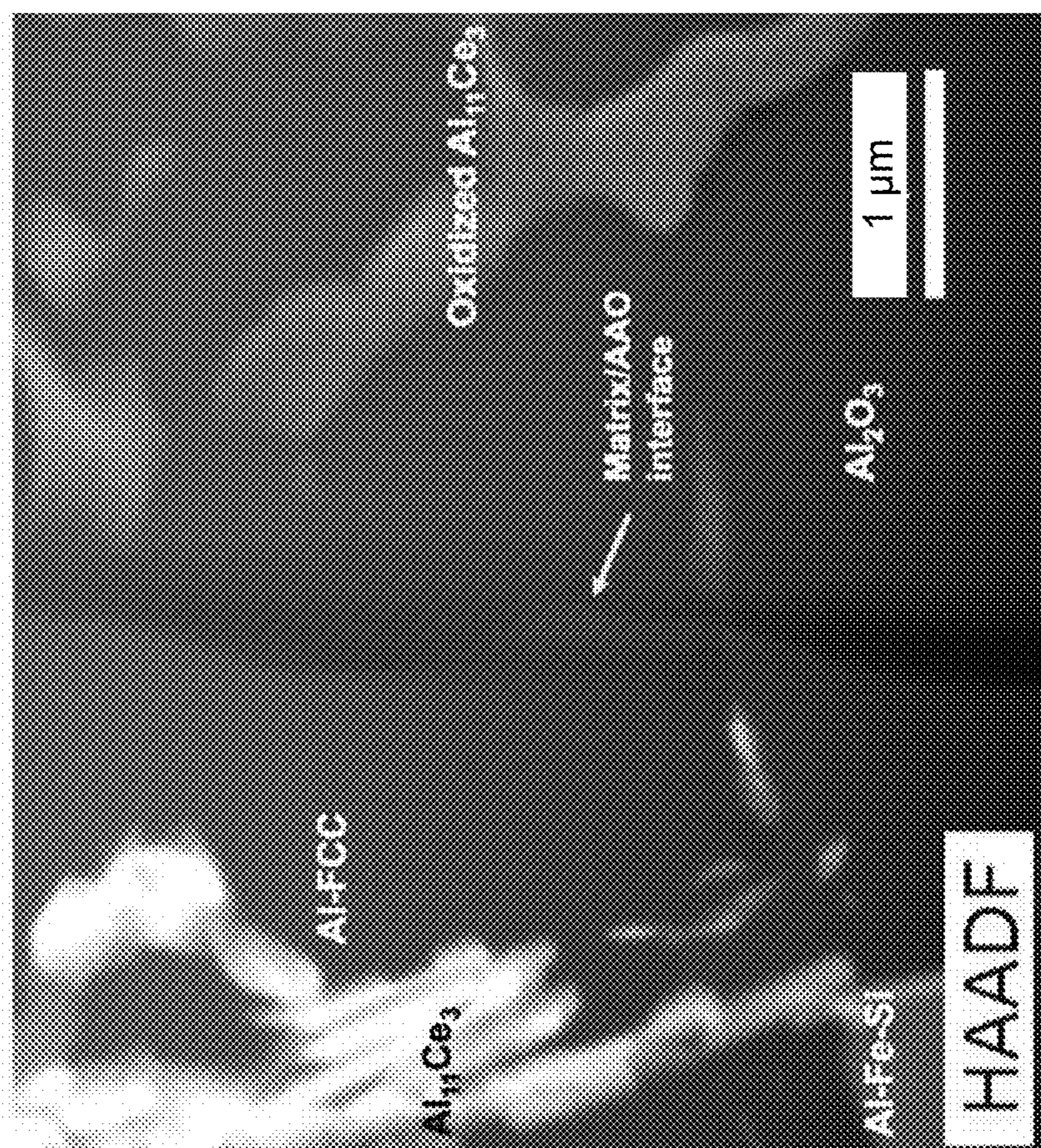


FIG. 12

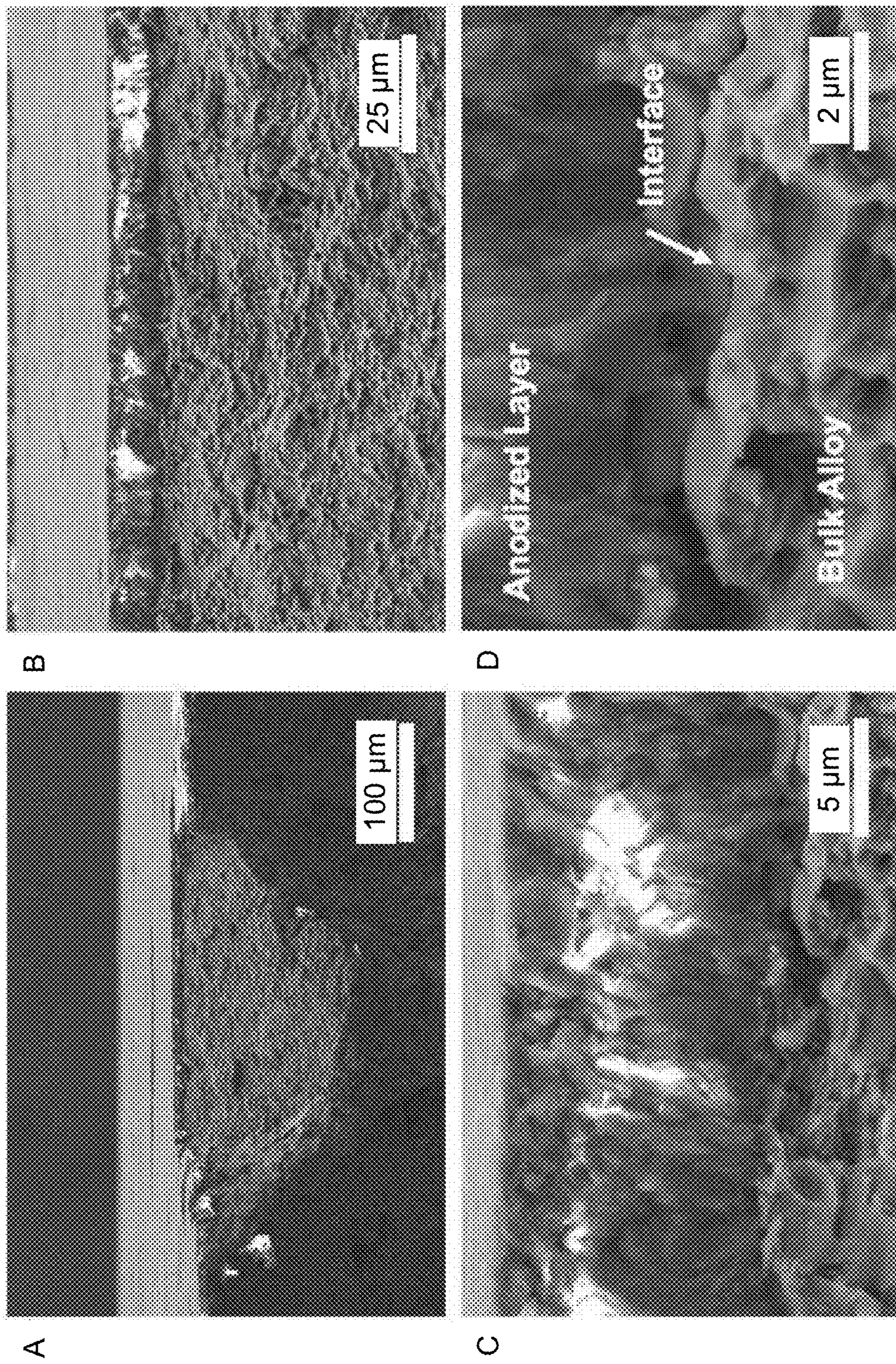


FIG. 13

**ENHANCED ANODIZATION  
FUNCTIONALITY IN AL-RARE EARTH  
ELEMENT-BASED ALLOYS**

RELATED APPLICATIONS

**[0001]** This application claims priority to Provisional U.S. Appl. No. 63/112,792 filed on Nov. 12, 2020, which is herein incorporated by reference.

**[0002]** This invention was made with Government support under Contract No. DE-AC52-07NA27344 awarded by the United States Department of Energy. This invention was also made with Government support under Contract No. DE-AC05-000R22725 awarded by the United States Department of Energy. The Government has certain rights in the invention.

FIELD OF THE INVENTION

**[0003]** The present invention relates to anodization functionality in alloys, and more particularly, this invention relates to anodization of Al-rare earth element-based alloys, such as Al—Ce-based alloys.

BACKGROUND

**[0004]** Aluminum alloys are highly valued in many applications for a number of reasons, including their resistance to corrosion. The natural resistance to corrosive attack of aluminum alloys comes from its ability to rapidly form a passivating oxide layer at the material surface which is highly noble and resistant to electrochemical attack.

**[0005]** The thickness of a naturally-formed oxide layer is generally between 10 to 100 angstroms depending on ambient conditions, thereby naturally offering limited corrosion resistance in highly corrosive environments such as those encountered in many structural applications. In order to produce a thicker oxide layer at the surface of the alloy, a process known as anodizing is used. Anodizing uses electrolytic solutions and a metallic cathode to form artificially thick oxide skins at the material surface. Type II anodizing utilizes sulfuric acid in varying concentrations as an electrolyte and produces layers of up to 25  $\mu\text{m}$  in thickness. The thicker oxide skin improves corrosion resistance and, in some cases, can be used to improve wear resistance of the alloy.

**[0006]** Aluminum alloys include additional elements which are added to acquire desired properties. The presence of these elements can have differing impacts on the anodization of aluminum alloys. For example, the 3xxx series of wrought alloys turn brown following anodization due to their manganese content. The presence of secondary constituent particles at or near the surface to be anodized is a concern. These particles often have a different electrochemical potential than the mostly aluminum matrix. This difference in chemical potential means secondary particles are often preferentially attacked leaving behind a porous network, weakening the overall oxide layer mechanical integrity. The Al-rare earth element (REE) alloy system presented herein has characteristic intermetallic phases which have higher stability and are thus retained longer in the oxide layer. The retention of these phases allows them to act as anchor sites to increase the oxide skin adhesion and prevent damage.

SUMMARY

**[0007]** A product, according to one aspect, includes an aluminum alloy having an anodized layer. The alloy has a bulk composition including at least 1 wt. % of one or more rare earth elements (REEs).

**[0008]** A product, according to another aspect, includes microstructures extending across a boundary defined between an anodized layer and an unoxidized alloy. Each microstructure includes an intermetallic phase transitioning to an oxidized intermetallic phase across the boundary.

**[0009]** A product, according to another aspect, includes an anodized layer where up to 90% of a thickness of the layer includes voids resulting at least in part from dissolution of a rare earth element oxidized intermetallic phase. The voids are in a morphology of the dissolved oxidized intermetallic phase.

**[0010]** Other aspects and advantages of the present invention will become apparent from the following detailed description, which, when taken in conjunction with the drawings, illustrate by way of example the principles of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

**[0011]** FIG. 1 is a schematic of a product, in accordance with one aspect of the present invention.

**[0012]** FIG. 2 is a schematic of a product, in accordance with one aspect of the present invention.

**[0013]** FIG. 3 are images of an as-anodized surface morphology of Al-12Ce-1Fe-0.4Mg alloy, in accordance with one aspect of the present invention.

**[0014]** FIG. 4 are images of the cross section of an anodized layer on Al-12Ce-1Fe-0.4Mg alloy prepared by polishing the surface, in accordance with one aspect of the present invention.

**[0015]** FIG. 5 are images of the cross section of an anodized layer on Al-12Ce-1Fe-0.4Mg alloy prepared by polishing the surface, in accordance with one aspect of the present invention.

**[0016]** FIG. 6 are images of the cross section of an anodized layer on Al-12Ce-1Fe-0.4Mg alloy prepared by polishing the surface, in accordance with one aspect of the present invention.

**[0017]** FIG. 7 are images of the cross section of an anodized layer on Al-12Ce-1Fe-0.4Mg alloy prepared by fracturing the surface, in accordance with one aspect of the present invention.

**[0018]** FIG. 8 are images of the cross section of an anodized layer on Al-12Ce-1Fe-0.4Mg alloy prepared by fracturing the surface, in accordance with one aspect of the present invention.

**[0019]** FIG. 9 is an annular dark-field in the scanning transmission (STEM ADF) micrograph of matrix and anodized layer, in accordance with one aspect of the present invention.

**[0020]** FIG. 10 is a STEM ADF micrograph of matrix and anodized layer with phases labeled, in accordance with one aspect of the present invention.

**[0021]** FIG. 11 are bright field transmission electron microscopy (TEM) micrographs of interface between base metal and anodized layer, in accordance with one aspect of the present invention.

**[0022]** FIG. 12 is a high angular annular dark field (HAADF) TEM image, in accordance with one aspect of the present invention.

**[0023]** FIG. 13 are SEM images of anodized layer and bulk alloy following mechanical fracture in tension showing the interface between the Al-REE alloy and the anodized aluminum oxide layer, in accordance with one aspect of the present invention.

#### DETAILED DESCRIPTION

**[0024]** The following description is made for the purpose of illustrating the general principles of the present invention and is not meant to limit the inventive concepts claimed herein. Further, particular features described herein can be used in combination with other described features in each of the various possible combinations and permutations.

**[0025]** Unless otherwise specifically defined herein, all terms are to be given their broadest possible interpretation including meanings implied from the specification as well as meanings understood by those skilled in the art and/or as defined in dictionaries, treatises, etc.

**[0026]** It must also be noted that, as used in the specification and the appended claims, the singular forms “a,” “an” and “the” include plural referents unless otherwise specified.

**[0027]** The following description discloses several preferred embodiments of an anodized Al—Ce based alloy and/or related products and methods.

**[0028]** In one general aspect, a product includes an aluminum alloy having an anodized layer. The alloy has a bulk composition including at least 1 wt. % of one or more rare earth elements (REEs).

**[0029]** In another general aspect, a product includes microstructures extending across a boundary defined between an anodized layer and an unoxidized alloy. Each microstructure includes an intermetallic phase transitioning to an oxidized intermetallic phase across the boundary.

**[0030]** In another general aspect, a product includes an anodized layer where up to 90% of a thickness of the layer includes voids resulting at least in part from dissolution of a rare earth element oxidized intermetallic phase. The voids are in a morphology of the dissolved oxidized intermetallic phase.

**[0031]** Anodizing produces corrosion resistant layer coatings for aluminum alloys. The process causes steady state growth of a thin protective oxide layer on the alloy. Anodizing may be used with most commercial aluminum alloys to increase material corrosion resistance, but often, the brittle, passive oxide layer formed during anodization does not adhere well to the material, reducing effectiveness, and overall compatibility. Despite anodization being an economical, mostly automated batch process capable of coating hundreds of parts in a single cycle; not all alloys are compatible. Al—Cu and Al—Zn alloys, for example, both exhibit high levels of ion entrainment in the anodizing layer resulting in uneven and limited growth, undesirable coloration, and poor adhesion to the alloy below the oxidation front.

**[0032]** Various aspects of the present disclosure describe the compatibility and effect of anodization for newly developed alloy Al-rare earth element (REE) alloys, including Al—Ce alloys. Al—Ce alloys are compatible with current processes and exhibit improved adhesion of the passivated layer where intermetallic phases anchor the anodized product to the unconverted bulk. At least some of the anodized

alloys described herein exhibit improved strain compatibility from the voids and anchoring, thereby enabling growth of relatively thicker layers without spalling than previously achievable. The combination of near-zero Ce solubility in face centered cubic (FCC) Al with the formation of a highly stable intermetallic provides Al—Ce alloys having several advantages over current commercial aluminum alloys. Al—Ce alloys may be manufactured using current foundry and manufacturer technology and infrastructure.

**[0033]** While much of the present description discusses Al—Ce as the primary example, it is to be understood that similar results are expected for alloys of Al with other REEs. Thus, an REE other than Ce, and any combination of REEs, are considered as substantially isomorphic with Ce, and such REE and/or REE combinations may be used with and/or in place of Ce in any of the various alloys described herein. For example, Al-REE alloys may include La, Nd, Pr, mischmetal, etc., or any combination thereof. Thus, the mention of Ce, and/or use of any particular Ce wt. % herein can be considered as referring to pure Ce, a different pure REE such as La or Nd, or an admixture of two or more REE that combines to the stated value at any ratio.

**[0034]** Al-REE alloys as presented herein may include at least one rare earth element, at least two rare earth elements, or any combination of rare earth elements including mischmetal. As used throughout the present disclosure, a “matrix” refers to the substantially pure Al phase, e.g., the FCC crystalline Al phase that is the primary phase constituent of Al alloys.

**[0035]** Rare earth elements as referred to herein may include yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu).

**[0036]** Natural mischmetal comprises, in terms of weight percent, about 50% cerium, 30% lanthanum, with the balance being other rare earth elements. Thus, modification of Al alloys with cerium through addition of mischmetal may be a less expensive alternative to pure cerium.

**[0037]** Al—Ce alloys are eutectic aluminum alloys which exhibit elevated thermal stability due to decreased mobility of the primary alloying addition in the aluminum matrix. Al—Ce alloys offer advantages like high castability, limited or no heat treatment requirements, and high-temperature strength retention. These alloys are characterized by the formation of networks of intermetallic phases during solidification that do not follow the same solutionization-reprecipitation pathway expected of most other aluminum structural alloys. The secondary phases formed during solidification may be of the binary or higher order type depending on the starting composition of the molten metal. Based on existing aluminum alloys and the effect secondary phases have on anodized layer integrity, it would be expected that the large volume fraction of intermetallic present in the alloy volume to be anodized would have a negative effect on layer integrity and adhesion. However, the inventors were surprised that the interconnected nature of the intermetallic features, their electrochemical stability, and high aspect ratios create an anchoring effect which increases layer adhesion and has the effect of strengthening the oxide layer against cracking, exfoliation, and spalling.

**[0038]** The chemical process of anodizing relies on the potential of aluminum to readily form stable oxides in the



presence of a bias current and electrolyte. In practice, there are three types of anodization. Chromic anodizing (Type I) produces thin and relatively brittle anodized coatings. This process is being phased out due largely to human health and environmental concerns related to the use of the chemicals required for the process. Sulfuric acid soft or transparent anodizing (Type II) is the type used in many of the exemplary aspects described herein. This process is used to produce films between 2  $\mu\text{m}$  and 25  $\mu\text{m}$  in thickness. These films are relatively transparent and can be easily dyed due to the celled pore structure formed during the anodizing process. Sulfuric acid hard or opaque anodizing (Type III) coatings are used when elevated wear and/or corrosion resistance are preferred. This process is very similar to that of Type II but instead produces thicker films which can be up to 150  $\mu\text{m}$  in thickness. Additionally, there are several niche anodizing practices which include organic acid, oxalic acid, and other electrolyte solutions.

**[0039]** Each of the above methods reduce the surface of the aluminum to produce an artificially thick oxide layer. All anodizing types are generally compatible with Al—Ce alloys and their network of interconnected secondary phase constituents for increased anodizing layer cohesion. The base alloy is preferably an alloy which comprises high contents of stable intermetallics which produce a 3-zone anodized surface where the partially oxidized precipitate acts as an anchoring site for the oxide layer, as described herein.

**[0040]** In various aspects of the present disclosure, a Type II transparent anodizing process may be used to produce a relatively thick passivated layer on the surface of an Al—Ce alloy. Various aspects of the present application may be applied in conjunction with any Type I, II, or III anodizing process to promote coating strength and stability. In an exemplary aspect, the Al—Ce alloy has a composition Al-12Ce-0.4Mg wt. %. In other approaches, the Al—Ce alloy has a composition Al-12Ce-1Fe-0.4Mg wt. %.

**[0041]** Compositions described throughout the present disclosure are in weight percent unless otherwise noted.

**[0042]** In one aspect, a product comprises an aluminum alloy (unoxidized bulk alloy) having an anodized layer formed thereon, the alloy having a bulk composition comprising at least 1 wt. % of one or more rare earth elements. The one or more rare earth elements may be any of the rare earth elements listed herein, or any combination thereof. The at least 1 wt. % preferably refers to a total weight percentage of rare earth elements. For example, in an alloy having a combination of rare earth elements, the total weight percentage of the rare earth elements in the alloy is at least 1 wt. %. In preferred aspects, the one or more rare earth element is present in a weight percentage of the bulk composition in a range of about 6% to about 12%. In other approaches, the one or more rare earth element is present in a weight percentage of the bulk composition in a range of about 2% to about 20%.

**[0043]** In at least some approaches, the aluminum-rare earth alloy comprises at least one additional element including silicon (Si), copper (Cu), iron (Fe), magnesium (Mg), zinc (Zn), lithium (Li), nickel (Ni), titanium (Ti), manganese (Mn), zirconium (Zr), or any combination thereof. In various aspects, the additional element may be present in a weight percentage of the bulk composition in a range of about 0% to about 10%.

**[0044]** In various aspects, the product comprises microstructures, at least some of which contain Al-RE-based intermetallic plates and/or rods that extend across a boundary defined between the anodized layer and an underlying unoxidized alloy. The microstructures may be in a range between about 1  $\mu\text{m}$  to about 20  $\mu\text{m}$  in major dimension and in a range between about 0.1  $\mu\text{m}$  to about 2  $\mu\text{m}$  in minor dimension in the underlying structure. The microstructures may exist as isolated structures. In some aspects, the microstructures are layered. In at least some aspects, said boundary is generally found at the oxidation front. Those microstructures that cross the boundary may include an intermetallic phase transitioning to an oxidized intermetallic phase across the boundary from the alloy to the anodized layer. The microstructures that cross the boundary act as anchors that enhance the adhesion of the anodized layer to the underlying bulk alloy (the unoxidized Al-REE alloy).

**[0045]** In at least some aspects, the anodized layer comprises a plurality of ceramic oxide phases. The plurality of ceramic oxide phases may include an Al-REE oxide phase and an aluminum oxide phase in an interconnected structure. In various approaches, the ceramic oxide phases include amorphous phases.

**[0046]** According to various aspects described herein, the anodized layer includes a first zone and a second zone. The anodization process of the Al-REE alloy described herein creates two zones in the anodized layer, as would become apparent to one having ordinary skill in the art upon reading the present disclosure. See, e.g., FIGS. 1-2 and accompanying description, below. The second zone is preferably positioned between the first zone and the alloy. The first zone, in at least some approaches, is an outermost layer (e.g., has an outer surface of the anodized layer). The second zone includes a rare earth element oxidized intermetallic phase. An “oxidized intermetallic” as used throughout the present disclosure may include any oxide-intermetallic formation resulting at least in part from the anodization of the aluminum-rare earth alloy as described herein. In one exemplary aspect, the second zone includes at least an oxidized matrix and an oxidized intermetallic (e.g., the REE oxidized intermetallic). The oxidized matrix may include aluminum oxide. The oxidized intermetallic may include, for example, a combination of aluminum oxide and cerium oxide where the unoxidized intermetallic once was,  $\text{Al}_{11}\text{Ce}_3$ , aluminum-cerium-oxide, etc., or any combination thereof. Oxidized regions of prior intermetallic particles may also include mixed oxides, complex oxides, oxides of variable stoichiometry, non-oxidized regions, etc.

**[0047]** In at least some approaches, the first zone includes voids having a morphology of the rare earth element oxidized intermetallic phase removed from the first zone. During the anodization process, the first and second zones are created concurrently, with the second zone growing faster than the first zone. For example, the REE oxidized intermetallics are created during anodization and then eventually become dissolved to create the voids in the first zone. The dissolution that creates the voids occurs during the anodization process, without the need to change the anodization process. The voids preferably are in the morphology of the dissolved oxidized intermetallic which retained the morphology of the unoxidized intermetallic phase in the base alloy microstructure. For example, the voids have a

morphology of a previously present rare earth element oxidized intermetallic phase removed from (e.g., dissolved out of) the first zone.

**[0048]** In various aspects, up to 90% of a thickness of the anodized layer includes the voids resulting at least in part from dissolution of a rare earth element oxidized intermetallic phase. For example, up to 90% of the thickness of the anodized layer may be the first zone as described herein.

**[0049]** In various approaches, the extent of the anodization is selectable by one having ordinary skill in the art in view of the intended application. According to various illustrative approaches, a total thickness of the anodized layer (e.g., including the first zone and the second zone) is in a range of about 0.1  $\mu\text{m}$  to about 300  $\mu\text{m}$ . A thickness of a first zone may be in a range of about 0.1  $\mu\text{m}$  to about 300  $\mu\text{m}$ . A thickness of a second zone may be in a range of about 0.1  $\mu\text{m}$  to about 300  $\mu\text{m}$ . A thickness of the bulk composition (e.g., the third zone) may be greater than or equal to 10  $\mu\text{m}$ . In various aspects, the first zone may comprise the whole thickness of the anodized layer. In other aspects, the second zone may comprise the whole thickness of the anodized layer. Any of the foregoing thicknesses may vary and be determinable by one having ordinary skill in the art in view of the intended application. The inventors were surprised to discover that even partial anodization of the Al-REE alloys resulted in the improved adhesion properties described herein.

**[0050]** In at least some approaches, the bulk composition is a third zone positioned below the second zone. The third zone may comprise the FCC matrix of the Al-REE alloy and an intermetallic phase (e.g.,  $\text{Al}_{11}\text{Ce}_3$ ). In various approaches, the third zone defines a boundary (e.g., extent) of the anodization process.

**[0051]** FIG. 1 is a schematic of an exemplary product, in accordance with one embodiment. As an option, the present product 100 may be implemented in conjunction with features from any other embodiment listed herein, such as those described with reference to the other FIGS. Of course, however, such product 100 and others presented herein may be used in various applications and/or in permutations which may or may not be specifically described in the illustrative embodiments listed herein. Further, the product 100 presented herein may be used in any desired environment.

**[0052]** As shown, FIG. 1 includes Zone 1 102 (e.g., the first zone), Zone 2 104 (e.g., the second zone), and Zone 3 106 (e.g., the third zone), as described in detail above, separated by imaginary boundaries shown by the dotted lines. Zone 1 102 includes voids 108 in an oxidized matrix 110. Zone 2 104 includes Al-REE oxidized intermetallic 112 present in the oxidized matrix 110. Zone 3 106 includes the bulk composition of the unoxidized alloy, which in this example includes Al-REE intermetallic 114 present in the FCC matrix 116.

**[0053]** FIG. 2 is a schematic of an exemplary product, in accordance with one embodiment. As an option, the present product 200 may be implemented in conjunction with features from any other embodiment listed herein, such as those described with reference to the other FIGS. Of course, however, such product 200 and others presented herein may be used in various applications and/or in permutations which may or may not be specifically described in the illustrative embodiments listed herein. Further, the product 200 presented herein may be used in any desired environment.

**[0054]** FIG. 2 includes many of the same features as those described in FIG. 1. It should be understood by one having ordinary skill in the art that similar numbering implies similar function, unless otherwise noted herein.

**[0055]** As shown, FIG. 2 includes a protective structure 201 having a construction similar to the product depicted in FIG. 1, coupled to a substrate 202 to form the larger composite product. In preferred aspects, the substrate 202 has a different composition than the alloy (e.g., the composition of the substrate 202 is different than the Al-REE alloy of the bulk composition described with respect to Zone 3 106). Zone 3 106 is coupled to an outer surface of the substrate 202, and/or vice versa, via a process known in the art. For example, the Al-REE alloy may be plated thereon, sputtered thereon, etc., before anodizing. The Al-REE alloy is preferably anodized to form a protective layer (e.g., comprising Zone 1 102, Zone 2 104, and Zone 3 106, or any combination thereof) on the substrate 202.

**[0056]** In another approach, the protective structure 201 is anodized completely through, e.g., only Zone 1 102 and Zone 2 104 are present on the substrate.

**[0057]** A substrate, according to various aspects, may include glass, a ceramic, another alloy, silicon, etc., as would be selectable by one having ordinary skill in the art in view of the intended application, upon reading the present disclosure. The substrate may be flexible or rigid, depending on the intended application. The substrate may be part of the final component for which the anodized Al-REE alloy is used. In other approaches, the substrate may be sacrificial, and the anodized Al-REE alloy may be removed therefrom before use in any of various intended applications.

**[0058]** In other approaches, the alloy may be applied to the substrate as a relatively thin layer (e.g., with a deposition thickness in a range of about 10  $\mu\text{m}$  to about 10 mm). In other approaches, the alloy may be formed as a bulk material piece coupled to the substrate or as a monolith product.

**[0059]** In various approaches, the extent of the anodization is selectable by one having ordinary skill in the art in view of the intended application. In preferred aspects, at least half of the deposition thickness of the Al-REE alloy is anodized (e.g., the first and second zones are formed in at least half of the total deposition thickness of the alloy). The inventors were surprised to discover that even partial anodization of the Al-REE alloys resulted in the improved adhesion properties described herein.

**[0060]** Referring to FIGS. 1-2 and other approaches, the initial microstructure of the Al-REE alloy may be tunable prior to the anodization for tuning the resulting anodization layer. For example, the Al-REE alloy may be thermomechanically processed (e.g., by extrusion, forging, rolling, cold spray, friction stir welding, etc.) for altering the composition and/or microstructure of the alloy, prior to the anodization, as would be determinable by one having ordinary skill in the art upon reading the present disclosure. The Al-REE alloys may be thermomechanically processed starting with a bulk cast billet, blank, etc. Other conventional methods for thermomechanically processing Al-REE alloys include using spray formed billets and consolidating powder into a monolithic piece of material through the process.

**[0061]** As previously noted, the anodizing process produces a network of pores at the surface of the alloy. In many approaches, an average diameter of each pore in solid solution alloys are in the range of about 10 nm to about 300 nm. It should be understood that “pores” as used throughout

the present disclosure refers to substantially cylindrical channels that run through the anodized layer along the growth direction that are formed in conventional anodization. The “voids” as used throughout the present disclosure are formed when the previously present Al-REE-based intermetallics dissolve (e.g., the voids are in the morphology of the intermetallics), as described in detail above. The voids have a similar morphology to previously present Al-REE-based intermetallics (e.g., the morphology of the intermetallics being plates, rods, particles, etc.). The anodized Al-REE alloys described herein may include a combination of pores and voids as would become apparent to one having ordinary skill in the art upon reading the present disclosure.

#### Experimental

**[0062]** Al—Ce Alloy Casting

**[0063]** An exemplary part was pulled from a batch of high-pressure die-cast Al-12Ce-1Fe-0.4Mg parts. The parts were produced using known methods.

**[0064]** Anodizing

**[0065]** The anodized coating was applied using a type II sulfuric acid process. The part was rinsed, etched, desmutted, and mounted to a universal rack before being anodized. Sulfuric acid was used as the electrolyte for the process with a constant DC voltage and circulated bath. Various parameters of the anodization process are within standard ranges and common operating conditions. For example, the rinse and etch agents, voltage, acid concentration, etc., may be determinable by one having ordinary skill in the art.

**[0066]** Microscopy

**[0067]** For imaging samples of the anodized alloy, both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed. Metallographic samples were sectioned using a low-speed saw, polished with standard metallurgical techniques, and mounted in hard epoxy resin. An accelerating voltage of 10 kV was used for SEM sample image capture in both secondary and backscatter electron modes. Imaging of the fractured surface used mounting of a fractured sample with conductive adhesive to an SEM sample plate.

**[0068]** For TEM analysis, a foil was extracted from the previously prepared SEM sample using focused ion beam (FIB) milling and the foil was then mounted to a TEM grid and imaged in both bright field and high angular annular dark-field mode.

**[0069]** FIG. 3 includes SEM images of the structure of an Al—Ce alloy where voids form following the preferential attack of the intermetallic constituents after being oxidized by the electrolyte. The images of the surface of the part show that the voids produced by intermetallic phase dissolution create a surface-spanning network of voids. The voids, like those imaged in cross section, retain the familiar morphology of eutectic  $\text{Al}_{11}\text{Ce}_3$  intermetallics. The voids are less than or equal to 5  $\mu\text{m}$  in length. An average width throughout the length of the void is about 2  $\mu\text{m}$ .

**[0070]** The voids vary in size but are on the order of about 250 nm to about 500 nm in thickness but are not cylindrical in nature. Thus, the voids shown in FIG. 3 images are not caused by the same diffusional process as cellular pores present in solid solution alloys. Though not as evenly distributed and larger in size than the pore structure of a solid solution alloy, the voids would still likely accept dye and other secondary coatings common in the anodizing industry.

**[0071]** FIG. 4-6 are scanning electron microscope (SEM) images of the anodized layer in a cross section view. The anodized skin is substantially uniform in thickness and overall integrity. Despite the anodized layer being populated with porosity where  $\text{Al}_{11}\text{Ce}_3$  intermetallic phases once existed, the layer maintains a uniform growth rate and excellent adhesion. The anchoring potential of the intermetallic phase are shown in FIGS. 4-6 where the partially oxidized laths of intermetallic phases extend into the oxide layer and are continuous with their unoxidized portions. This continuity crosses into the matrix anchoring the oxide skin to the bulk material. The anchoring of the layer via continuous intermetallic laths increases layer wear resistance and reduces the effect of anodizing on fatigue life of aluminum alloys.

**[0072]** A concern in applying an anodized coating to aluminum is the integrity of the coating in the presence of mechanical stresses. Since the anodized layer is composed of brittle ceramic compounds, cracks can readily form which quickly travel and produce spalling of the oxide layer, reducing wear and corrosion resistance. To test the propensity for the oxide layer to crack and separate from the bulk material, parts were fractured using a bending force with the oxide layer being on the tension face of the bend test. FIGS. 7 and 8 are SEM images of the fracture surface. The ceramic oxide layer exhibits brittle fracture with cleavage faces being observed along the surface. In contrast, the bulk alloy material fractures with ductile characteristics related to micro void coalescence in open mode stress. This difference in fracture mechanisms leads to, in some places, crack propagation into the bulk material which is blunted and slowed by ductile fracture action (See inset of FIG. 7 Part B). In some cases, the crack propagation is stopped directly at the oxide-alloy interface (See inset of FIG. 8 Part B). Additionally, despite the brittle nature of the oxide fracture and crack propagation, no observable separation of the oxide skin from the bulk alloy is observed along the fracture surface. Also, no visible cracks propagate along the oxide surface. The lack of visible cracks along the oxide surface enables any damage induced spalling during service lifetimes to be localized to the damage site and would not extend beyond, resulting in retention of majority of anodized surface and its accompanying benefits.

**[0073]** Results

**[0074]** Al—Ce Anodized Layer Characteristics

**[0075]** Following anodization, the part was sectioned and mounted in cross-section for easy viewing of the anodized layer as shown in the SEM images of FIG. 4-6. The anodized aluminum oxide (AAO) layer thickness is substantially uniform and on the order of about 10  $\mu\text{m}$  to about 15  $\mu\text{m}$  thick throughout. The high concentration of intermetallic phases, oxidize followed by selective corrosive attack. Within the AAO are a number of impurity particles which do not appear to affect the overall layer thickness. The composition of these particles varies with some being primary intermetallics of  $\text{Al}_{11}\text{Ce}_3$  while others are ternary intermetallics (Al—Fe—Si or Al—Ce—Fe) or impurities from the industrial die-casting process.

**[0076]** A transmission electron microscope (TEM) was used to provide greater insight into phase formation and coherency of the mixed phase oxide layer and bulk alloy. FIG. 9 is an annular dark field (ADF) image of sample taken from the interface of the alloy and oxide skin. A clean and sound interface with the unoxidized bulk alloy and two

distinct zones within the AAO are shown. Three distinct areas are identifiable in the image. Zone 1 starting from the exterior oxide surface shows an oxide skin composed of  $\text{Al}_2\text{O}_3$  ceramic with a void network where previously existed interconnected laths of  $\text{Al}_{11}\text{Ce}_3$ . The oxidized particles are selectively removed during anodization closer to the external AAO surface and form the network of voids of the same morphology as the oxidized intermetallic particles. Zone 2 is the area of the oxide skin where void formation has not yet occurred, and multiple oxide compounds coexist. Zone 2 includes oxidized intermetallic particles in combination with anodized aluminum matrix. This region is the source of the anchoring potential of the oxide skin. The production of a Zone 2 is possible because the oxide growth front leads selective intermetallic dissolution and void formation by 5  $\mu\text{m}$  on average. The oxidized intermetallics extend across the interface and are adhered to their unoxidized portions in the sample bulk creating the anchoring effect. Oxidation of the intermetallic particles at the interface propagates at the same rate as the aluminum matrix, resulting in a substantially uniform AAO thickness. Zone 3 is the bulk unoxidized alloy.

[0077] FIG. 10 is the compositional analysis of phases from both the anodized layer and alloy bulk. The bulk phases show expected compositions with the matrix being nearly pure aluminum with some magnesium in solid solution and multiple intermetallic phases. The anodized layer exhibits a mixture of oxides including  $\text{Al}_2\text{O}_3$ , the reaction product of the anodizing process, and a mixed oxide rich in the REE element cerium. This oxide has a mixed phase structure which along with possible transmission effects accounts for the reduction in relative cerium content when compared to the bulk composition. Bright field images (FIG. 11) show the structure of the interface and how intermetallic laths remain semi coherent with mixed oxide compounds across the anodizing boundary.

[0078] The expected  $\text{Al}_{11}\text{Ce}_3$  phase is present, point compositions can be found in Table 1, in the Al-12Ce-1Fe-0.4Mg bulk alloy alongside the high purity aluminum matrix with a small amount of O and Mg dissolved within. The AAO exhibits oxidized phases of each constituent present in the bulk alloy: Al(FCC),  $\text{Al}_{11}\text{Ce}_3$ , and Al—Fe—Si phases. Within the oxidized  $\text{Al}_{11}\text{Ce}_3$ , there is a reduced concentration of Ce compared to the phases unoxidized stoichiometry. The result is reflective of the selective removal of Ce in  $\text{Al}_{11}\text{Ce}_3$  during the anodization process. Additionally, ternary Al—Fe—Si phases are present which form throughout the sample and have a long needle-like morphology.

TABLE 1

Compositions of point scans taken from the phases of interest from FIG. 11.						
	O	Mg	Al	Si	Fe	Ce
Bulk Alloy (at. %)						
Al-FCC	1.3	1.1	97.6	0.0	—	0.0
Al—Fe—Si	6.6	0.4	71.7	6.1	14.8	0.3
$\text{Al}_{11}\text{Ce}_3$	0.6	0.1	69.7	11.7	0.0	17.9
Anodized layer (at. %)						
$\text{Al}_2\text{O}_3$	61.2	0.2	38.3	0.3	0.0	0.0
Oxidized $\text{Al}_{11}\text{Ce}_3$	62.7	0.1	32.9	1.9	0.0	2.4

[0079] The striations within the anodized layer (e.g., likely aligned columnar pores) appear to grow perpendicular to the surface of the bulk alloy and show variation in the growth direction at grain boundaries and surface imperfections. Selected area diffraction (SAD) of the AAO (See right insert of FIG. 11 part A) reveals an amorphous structure, while SAD of the bulk alloy shows distinct long-range crystalline order as expected (See left insert of FIG. 11 part A). The AAO cell structure appears to include propagation of pores unimpeded through a number of the oxidized intermetallic phases and/or grooving of the intermetallic phase due to the selective dissolution of cerium during the anodization process.

[0080] FIG. 12 is an image showing a clear interface between the AAO on the right and the bulk alloy on the left. The anodized layer is rich in O and both the Al—Fe—Si and  $\text{Al}_{11}\text{Ce}_3$  phases partially oxidize along the interface leading to multiple amorphous oxide composition with the AAO.

[0081] Failure Mode of the AAO and Bulk Alloy

[0082] To study how the AAO layer would affect material fracture, a section of the anodized part was cut, and a section then mechanically fractured in bending tension. Following fracture, the sample was mounted for SEM and imaged (FIG. 13). SEM images of the fractured section show the difference in fracture behavior between the bulk alloy and AAO. Pervasive throughout the bulk alloy is dimpling fracture, a characteristic ductile failure mode. However, the AAO exhibits signs of brittle fracture as expected being an amorphous ceramic. At the interface between AAO and bulk alloy (FIG. 13 part D). There exists a transition zone between fracture modes where the bulk alloy shows high plasticity and the AAO exhibits brittle fracture. The holes near the interface may be a result of changing crack propagation or pull out of partially oxidized intermetallics which protruded into the AAO.

[0083] The planar growth front, staggered mixed oxide dissolution, and coherency of the oxide-intermetallic boundary layer produces a material system with increased anodized oxide layer cohesion. This increased cohesion of the oxide layer to the bulk alloy decreases the likelihood of spalling and exfoliation while also decreasing the negative effects of anodizing on alloy fatigue performance.

[0084] Discussion

[0085] The structure, mechanical properties, and growth of the AAO in Al-12Ce-1Fe-0.4Mg include unique features. The high content of anodic intermetallic,  $\text{Al}_{11}\text{Ce}_3$ , in the path of the propagating oxide growth front resulted in large portions of the oxide layer being mixed in nature. The more anodic nature of the intermetallics also resulted in preferential dissolution during anodizing, leaving a large number of voids near the surface. The size and distribution of the pore network may impact the dye and coating process which is often used in anodizing. The process relies on a uniformly distributed network of nanopores to create an even, wear-resistant pigmentation at the alloy surface.

[0086] The lack of spalling and delamination of the AAO when fractured in tension likely results from the smooth transition between the AAO and bulk alloy. The protrusion of the hard intermetallics across the interface into the AAO creates an anchoring effect which prevents the separation of the layers during tension. The anchoring of the AAO to the bulk alloy improves the toughness and wear resistance, reduces spalling of the protective AAO layer, etc.

**[0087]** The anodized part exhibits a uniform anodizing layer growth and no major defects which conventionally affect Al alloys. Extensions of hard intermetallic phases into the AAO layer may improve adhesion and result in higher wear resistance and fracture toughness of the AAO. A large network of voids near the surface due to the selective anodic dissolution of Ce-rich intermetallics may have an impact on dyeability and other post anodizing coating procedures.

**[0088]** In Use

**[0089]** Anodizing of materials, as described herein, would be beneficial in several fields of application such as aerospace and marine applications, where increased corrosion resistance and paint adhesion are important factors in material selection. Various products described herein may be used in bond coating applications for improved adhesion to oxides, as a thermal barrier coating, to reduce electric conductivity, etc.

**[0090]** Anodized Al-REE alloys as described herein are of interest for transportation applications and reciprocating components. Anodized Al-REE alloys as described herein are of particular interest for turbocharger applications. At least some aspects of the anodized Al-REE alloys described herein may be configured for use in internal combustion engines (e.g., pistons, rods, etc.), aerospace (e.g., jet engine components, leading edge structures, heat resistant spacecraft components, etc.), and defense applications.

**[0091]** Anodized Al-REE alloys may be configured for use commercially in transportation, electricity, generation, industrial sectors, etc. The anodized Al-REE alloys presented herein may be used in current and future applications in the aerospace and power generation industries.

**[0092]** Additional applications for the anodized Al-REE alloys presented herein include turbine blades in gas turbine components, turbocharger components, combustion chamber components, exhaust system components, control surfaces, reaction vessel components, power generation components, steam turbine components, diverter components, diverse nozzle components, solar thermal collection components, high temperature wiring, etc.

**[0093]** The inventive concepts disclosed herein have been presented by way of example to illustrate the myriad features thereof in a plurality of illustrative scenarios, embodiments, and/or implementations. It should be appreciated that the concepts generally disclosed are to be considered as modular, and may be implemented in any combination, permutation, or synthesis thereof. In addition, any modification, alteration, or equivalent of the presently disclosed features, functions, and concepts that would be appreciated by a person having ordinary skill in the art upon reading the instant descriptions should also be considered within the scope of this disclosure.

**[0094]** While various embodiments have been described above, it should be understood that they have been presented by way of example only, and not limitation. Thus, the breadth and scope of an embodiment of the present invention should not be limited by any of the above-described exemplary embodiments, but should be defined only in accordance with the following claims and their equivalents.

What is claimed is:

1. A product, the product comprising:

an aluminum alloy having an anodized layer,

the alloy having a bulk composition comprising at least 1 wt. % of one or more rare earth elements (REEs).

2. The product of claim 1, the bulk composition comprising at least one additional element selected from the group consisting of: silicon (Si), copper (Cu), iron (Fe), magnesium (Mg), zinc (Zn), lithium (Li), nickel (Ni), titanium (Ti), manganese (Mn), and zirconium (Zr).

3. The product of claim 2, wherein the at least one additional element is present in a weight percentage of the bulk composition in a range of greater than 0% to about 10%.

4. The product of claim 1, wherein the one or more rare earth elements includes cerium (Ce).

5. The product of claim 1, wherein at least one of the one or more rare earth elements is selected from the group consisting of: yttrium (Y), lanthanum (La), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), and mischmetal.

6. The product of claim 1, wherein the one or more rare earth element is present in a weight percentage of the bulk composition in a range of about 6% to about 12%.

7. The product of claim 1, wherein the one or more rare earth element is present in a weight percentage of the bulk composition in a range of about 2% to about 20%.

8. The product of claim 1, wherein up to 90% of a thickness of the anodized layer comprises voids resulting at least in part from dissolution of a rare earth element oxidized intermetallic phase, the voids being in a morphology of the dissolved oxidized intermetallic phase.

9. The product of claim 1, wherein the anodized layer comprises first and second zones, the second zone being positioned between the first zone and the alloy, the first zone having voids having a morphology of a rare earth element oxidized intermetallic phase removed from the first zone, the second zone having the rare earth element oxidized intermetallic phase.

10. The product of claim 1, comprising a substrate having a different composition than the alloy, wherein the alloy is coupled to an outer surface of the substrate.

11. A product, the product comprising:

microstructures extending across a boundary defined between an anodized layer and an unoxidized alloy, each microstructure comprising an intermetallic phase transitioning to an oxidized intermetallic phase across the boundary.

12. The product of claim 11, wherein the anodized layer comprises a plurality of ceramic oxide phases, the plurality of ceramic oxide phases comprising an aluminum-rare earth element oxide phase and an aluminum oxide phase in an interconnected structure.

13. The product of claim 12, wherein the ceramic oxide phases include amorphous phases.

14. The product of claim 12, comprising a substrate having a different composition than the alloy, wherein the alloy is coupled to an outer surface of the substrate.

15. The product of claim 12, wherein the anodized layer comprises first and second zones, the second zone being positioned between the first zone and the alloy, the first zone having voids having a morphology of a rare earth element oxidized intermetallic phase removed from the first zone, the second zone having the rare earth element oxidized intermetallic phase.

**16.** A product, the product comprising:  
an anodized layer where up to 90% of a thickness of the layer comprises voids resulting at least in part from dissolution of a rare earth element oxidized intermetallic phase, the voids being in a morphology of the dissolved oxidized intermetallic phase.

**17.** The product of claim **16**, wherein the anodized layer has a composition characteristic of anodization of an alloy having a bulk composition comprising at least 1 wt. % of one or more earth elements (REEs).

**18.** The product of claim **17**, wherein at least one of the one or more rare earth elements is selected from the group consisting of: yttrium (Y), lanthanum (La), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), and mischmetal.

**19.** The product of claim **17**, comprising a substrate having a different composition than the alloy, wherein the alloy is coupled to an outer surface of the substrate.

**20.** The product of claim **17**, wherein the anodized layer comprises first and second zones, the second zone being positioned between the first zone and the alloy, the first zone having voids having a morphology of a rare earth element oxidized intermetallic phase removed from the first zone, the second zone having the rare earth element oxidized intermetallic phase.

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