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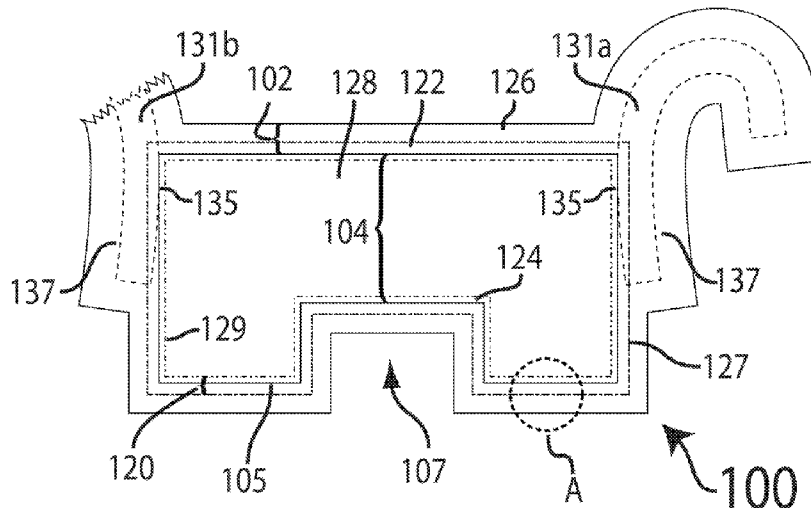


FIG. 1

(57) Abstract: Functionally coated objects include a metallic core part, a functional surface layer, and an interface layer, thus improving corrosion resistance or other functionality of the object relative to its core material. The core material may be metallic and may include nickel, and the surface layer may contain a refractory metal, such as tantalum. The interface layer is located between an unmodified portion of the surface layer and an unmodified portion the core material. A carbon seed layer is deposited onto the outer surface of the core part and the functional surface layer is subsequently deposited onto or partially simultaneously deposited with a carbon seed layer. The carbon seed layer may become part of the interface layer and may help create a diffusion barrier.

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OBJECTS HAVING A FUNCTIONAL SURFACE LAYER AND METHODS FOR MAKING THEM

TECHNICAL FIELD

[0001] This disclosure relates generally to methods for improving the surface characteristics of metallic objects. More specifically, this disclosure relates to objects having a metallic core and a functional surface layer, and methods for making such objects.

BACKGROUND

[0002] Objects to be positioned in corrosive environments frequently include a corrosion resistant outer surface in order to protect the object and to increase its usable service life. A corrosion resistant outer surface may be provided by manufacturing the entire object from a corrosion resistant material. Alternatively, a material may be applied to provide a functional coating on the object, providing, e.g., a corrosion resistant outer surface and/or enhanced biocompatibility. This coating (sometimes called cladding) is typically made from a material that is more corrosion resistant than the material from which the core of the object is made.

[0003] An applied surface layer should be tightly bound to the core material to withstand any mechanical and/or thermal shock the object might encounter during its utilization. In addition, the applied surface layer should not contain pinholes that might immediately expose the core to a corrosive environment. In some instances, a single pinhole can lead to the surface layer mechanically de-bonding (separating) from the core material over an area 100 times or more than the surface area of the pinhole in days or weeks. Once the surface layer starts to de-bond, it may bubble up in the vicinity of the pinhole, thus making the object prone to further wear and tear, and increasing the potential for a further increase in the corrosion attack area. Eventually, even a single pinhole as a starting point for a corrosion attack may lead to a full corrosion attack of the total underlying core of the object.

SUMMARY

[0004] Coated parts in accordance with the present disclosure include a core part overcoated with a functional surface layer. A carbon-based seed layer is applied to the core part before deposition of the functional surface layer. The core part includes an unmodified portion and may include a modified layer. The surface layer includes both an unmodified portion and a modified layer (often also called a diffusion layer) in contact with the unmodified portion or the modified layer (if it exists) of the core part. An interface layer includes the modified layer of the surface layer and, where it exists, the modified layer of the core part. The interface layer may be thinner and/or include no, a thinner, and/or less porous modified layer in objects made by the present processes that include applying a carbon-based seed layer compared to objects made of the same materials made where no carbon-based seed layer is employed. In embodiments, the interface layer may have a thickness in the range of about 0.5 μm to about 10 μm . The interface layer may improve adhesion between the functional surface layer and the core part.

[0005] In embodiments, the core part is made at least in part from a metallic composition (sometimes referred to herein as the “metallic core material”). In embodiments, the core part is made at least in part from a composition that includes nickel (Ni). In embodiments, Ni constitutes greater than about 15% of the metallic core material by weight. In embodiments, the metallic core material includes a Ni-alloy containing at least about 40% Ni by weight. In embodiments, the metallic core material includes a Ni-alloy containing from about 40% Ni to about 70% Ni by weight. In embodiments, the core part is made at least in part from a Ni-alloy containing from about 50% Ni to about 60% Ni by weight. In embodiments, the metallic core material includes a Ni-alloy containing chromium, molybdenum, and greater than about 40% Ni by weight. In embodiments, the metallic core material includes a Ni-alloy containing chromium, molybdenum, and from about 50% Ni to about 60% Ni by weight. In embodiments, the metallic core material is 100% Ni.

[0006] In other embodiments, the core part is made at least in part from a metallic composition that includes titanium (Ti). In embodiments, Ti constitutes greater than about 15% of the metallic core material by weight. In embodiments, the metallic core material includes a Ti-alloy containing at least about 40% Ti by weight. In embodiments, the metallic core material includes a Ti-alloy

containing at least about 80% Ti by weight. In embodiments, the metallic core material is from about 90% Ti to about 100% Ti by weight.

[0007] In embodiments, the functional surface layer is made from a composition that includes a refractory metal. In embodiments, the refractory metal constitutes greater than about 80% of the unmodified portion of the functional surface layer by weight. In embodiments, the refractory metal is tantalum (Ta). In embodiments, tantalum constitutes greater than about 80% of the unmodified portion of the functional surface layer by weight. In embodiments, the functional surface layer includes a metal selected from tantalum (Ta), niobium (Nb), molybdenum (Mo), tungsten (W), titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (Va), chromium (Cr), ruthenium (Ru), rhenium (Rh), osmium (Os), iridium (Ir), platinum (Pt), or an alloy containing one or more of these metals. In embodiments, the unmodified portion of the functional surface layer includes an alloy containing at least about 10% by weight of one or more of tantalum (Ta), niobium (Nb), molybdenum (Mo), tungsten (W), titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (Va), chromium (Cr), ruthenium (Ru), rhenium (Rh), osmium (Os), iridium (Ir), or platinum (Pt). In embodiments, the functional surface layer has a thickness of greater than about 10 μm . In embodiments, the functional surface layer has a thickness of greater than about 20 μm . In embodiments, the functional surface layer is substantially pinhole free.

[0008] In embodiments, the interface layer may be at least about 1.3 times thinner in objects made by the present processes that include applying a carbon-based seed layer compared to objects made where no carbon-based seed layer is employed. In embodiments, the interface layer may be from about 1.3 times to about 10 times thinner in objects made by the present processes that include applying a carbon-based seed layer compared to objects made where no carbon-based seed layer is employed. In embodiments, the interface layer may be from about 2 times to about 10 times thinner in objects made by the present processes that include applying a carbon-based seed layer compared to objects made where no carbon-based seed layer is employed. In embodiments, the interface layer may be from about 3 times to about 8 times thinner in objects made by the present processes that include applying a carbon-based seed layer compared to objects made where no carbon-based seed layer is employed. In embodiments, the interface layer may be from about 4 times to about 6 times thinner in objects made by the present processes that include applying a carbon-based seed layer compared to objects made where no carbon-based seed layer is employed.

[0009] In another aspect, the present disclosure relates to methods for making objects having a functional surface layer. The methods include applying a carbon-based seed layer to coat at least a portion of a core part and then depositing a functional surface layer on at least a portion of the carbon-coated portion of the core part. In embodiments, the carbon-based seed layer is deposited by chemical vapor deposition.

[0010] In embodiments, the method further includes cleaning the core part before applying the carbon-based seed layer. In embodiments, the method includes mounting the core part in a reactor before applying the carbon-based seed layer. In embodiments, the core part includes a wire and mounting the core part in a reactor includes hanging the core object by the wire. In embodiments, the method further includes spot welding a wire to the core part. In embodiments, the wire is a Ta wire. In embodiments, the method further includes removing at least a portion of the wire after deposition of the functional surface layer without disturbing the functional surface layer.

[0011] In embodiments, the carbon-based seed layer is applied at a thickness of from about 50 nm to about 5,000 nm. In embodiments, the carbon-based seed layer is applied at a thickness of from about 100 nm to about 2,000 nm. In embodiments, the carbon-based seed layer is applied at a thickness from about 200 nm to about 500 nm. In embodiments, the carbon-based seed layer applied to the core material contains at least about fifty atomic percent carbon. In embodiments, the carbon-based seed layer applied to the core material contains at least about ninety atomic percent carbon. For example, where the composition of the carbon-based seed layer is C_xM_y , where M is any element or combination of elements, the atomic percent is defined as $x/(x+y)*100$.

[0012] In embodiments, the method further includes transferring the carbon-coated core part to a reactor configured to deposit the functional surface layer on the carbon-coated core part. In embodiments, the carbon-based seed layer and functional surface layer are applied in the same reactor. In embodiments, the functional surface layer is deposited by a method selected from the group of chemical vapor deposition and salt bath electro deposition.

[0013] In embodiments, the portion of the core part to which the carbon-based seed layer is applied is made from a material that includes nickel (Ni), and depositing the functional surface layer on the carbon-coated core part includes forming a tantalum-containing composition on the carbon-coated core part. In embodiments, the portion of the core part to which the carbon-based seed layer

is applied is made from a material that includes titanium (Ti), and depositing the functional surface layer on the carbon-coated core part includes forming a tantalum-containing composition on the carbon-coated core part.

[0014] Use of a carbon-based seed layer in accordance with the present disclosure may reduce or eliminate the negative impact on corrosion resistance and/or biocompatibility resulting from the diffusion of atoms that can occur when a functional surface layer is applied directly to a metallic core part at high process temperatures via an electrodeposition salt bath or chemical vapor deposition process. When two distinct materials, such as two metals, are placed next to each other at elevated temperatures (such as when a functional surface layer is deposited by chemical vapor deposition directly on a metallic core part), diffusion may take place between the materials (sometimes also resulting in the creation of a porous sublayer, often referred to as a Kirkendall effect when discussed in relation to the diffusion between two metal materials). In general, the diffusion coefficients of the two materials (or at least some components of each material) in each other will not be the same. Accordingly, the flux of atoms from the components of the material with the higher diffusion coefficient will be larger, so there will be a net flux of atoms from the material having at least one component with a higher diffusion coefficient into the other material having components with a lower diffusion coefficient. This asymmetric flux of different atoms, when excessive, may result in the creation of a porous layer (Kirkendall porosity). The creation of a porous sublayer inside the interface layer generally weakens the adherence of the surface layer and increases the susceptibility of the interface layer to lateral corrosion (i.e., corrosion along the interface layer “plane”) after a pinhole has been established through the unmodified portion of the functional surface layer. A weaker adherence and/or a more brittle interface layer can lead to local mechanical failure between the functional surface layer and the core part, for example when the object is exposed to tensile or mechanical stress (e.g., due to flexing the object during use and/or installation) or when the object experiences thermal differential expansion stress. Reducing or eliminating the impact of out-diffusion of a material, such as nickel, from the core material using a carbon-based seed layer in accordance with the present disclosure may functionally improve the object by, for example, increasing the corrosion resistance or biocompatibility of the object. Other functional improvements may also be provided by the presently disclosed coatings, like an increase of the ductility of the resulting diffusion and/or interface layer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] The above and other aspects, features, and advantages of the present coated objects and the present methods of making them will become more apparent in light of the following detailed description when taken in conjunction with the accompanying drawings in which:

[0016] FIG. 1 schematically shows an illustrative functionally coated object in accordance with an embodiment of this disclosure;

[0017] FIG. 1A schematically shows the structure in the area defined by circle “A” of the illustrative object of Fig. 1;

[0018] FIG. 2 schematically shows an illustrative functionally coated object in accordance with another embodiment of this disclosure;

[0019] FIG. 2A schematically shows the structure in the area defined by circle “A” of the illustrative object of Fig. 2;

[0020] FIG. 3 is a flow-chart showing the steps of illustrative methods in accordance with the present disclosure;

[0021] FIG. 4 shows a SEM image of cross section of the object prepared as described in Example 1, having a Ta film deposited over a HASTELLOY® C-276 core part that was previously coated with a carbon-based seed layer in accordance with the present disclosure;

[0022] FIG. 5 is an EDX line scan for the object prepared as described in Example 1 showing the relative concentration change of various elements as a function of the distance from the original surface of the object;

[0023] FIG. 6 shows a SEM image of cross section of the object prepared as described in the Comparative Example A, below, having a Ta film deposited directly over a HASTELLOY® C-276 core part (i.e., a core part that was not previously coated with a carbon-based seed layer); and

[0024] FIG. 7 is an EDX line scan for the object prepared as described in Comparative Example A showing the relative concentration change of various elements as a function of the distance from the original surface of the object.

DETAILED DESCRIPTION

[0025] Particular embodiments of the present coated objects are described hereinbelow with reference to the accompanying drawings; however, it is to be understood that the disclosed embodiments are merely exemplary of the disclosure and the present coated objects may be embodied in various forms. One skilled in the art will readily recognize from the following discussion that alternative embodiments of the structures and methods illustrated herein may be employed without departing from the principles of the present disclosure described herein. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting, but merely as a basis for the claims and as a representative basis for teaching one skilled in the art to variously employ the concepts of the present disclosure in virtually any appropriately detailed structure.

[0026] As used herein, the term “about” means plus or minus 10% of the referenced number.

[0027] FIG. 1 shows an illustrative embodiment of a coated object 100 in accordance with the present disclosure having a functional surface layer 102 that fully encloses (encapsulates) a core part 104. Core part 104 has a complex geometry including a recess 107 and an outer surface 105 defining a corrosion fluid and/or biomaterial contact area. For example, recess 107 represents a blind threaded mounting hole. Surface layer 102 fully encloses outer surface 105 and is separated into an unmodified portion 126 and a modified layer 122, marked by an inner transition surface 127. Core part 104 is separated by a transition surface 129 into an unmodified portion 128 and may include a modified layer 124 (FIG. 1 shows the case when such a modified layer 124 is present). In embodiments, modified layer 124 may be de minimis or non-existent (as in the embodiment of FIG. 2, for example). Together, modified layer 122 and modified layer 124 (if present) form an interface layer 120 that is in intimate and bonded contact with transition surface 127 and transition surface 129. Alternatively, modified layer 122 forms a respective interface layer 120 that is in intimate and bonded contact with transition surface 127 and core part outer surface 105 in the case where the modified layer 124 is practically non-existent.

[0028] As the functional surface layer 102 is deposited, interface layer 120 is simultaneously created due to the high temperature process requirements needed for depositing a functional surface layer of a suitable thickness that is substantially pinhole free and able to substantially uniformly coat a complex surface without direct line of site access, for example including a part having a recess 107. In embodiments, a dense (i.e. non-porous) gradient diffusion bond layer may form in the modified layer 122 of the functional surface layer 102 with a gradient concentration transition of the material of the surface layer from high (close to about 90% near the transition surface 127) to low (less than about 10% near the interface between the modified surface layer 122 and the original outer surface 105 of part 104). At least one secondary gradient material component of the diffusion bond layer may be provided from the modified layer 124 of the core part 104, such that the secondary gradient material is highly concentrated near the original outer surface 105 and at a low concentration (less than about 10%) near transition surface 127.

[0029] Wires 131a, b, made from a substantially similar material as unmodified outer surface layer 126, are optionally secured (e.g., spot-welded) locally near their wire endings 135 to core part 104. The endings 135 and the immediate neighborhood of each wire 131a, b are fully encapsulated by unmodified outer surface layer 126 in such a way that wires 131a, b, and unmodified outer surface layer 126 bond together with a diffusion bond into a single material with no distinguishable boundary layer between outer surface 137 of wires 131a, b and transition surface 127 of surface layer 102, thus providing a pinhole free encapsulation of core part 104 and wire ending 135. The location where the wire ending 135 is secured may be chosen to be in an area of core part outer surface 105 outside any surface area that is intended to be sealed during usage of object 100 or in an area that does not have a high probability of experiencing wear and tear. Additionally, the location may be near a surface location where the wire ending 135 does not interfere with any intended mechanical motion function (for example, the wire should not be secured to a sealing surface of a ball valve, a sealing flange of a chemical reactor vessel, a propeller part exposed to fluid flow, etc.).

[0030] FIG. 1 shows unclipped wire 131a while it is still long enough to hang the part within a reactor for deposition of layers on the part. Hanging can be accomplished, for example, by bending wire 131a into a hook, twisting it around a support beam, or attaching it to another fixture (wire, clamp, holder, etc.). Wire 131b is shown to be clipped near, but outside surface layer 102 in such

a way that surface layer 102 is not disturbed mechanically. Since unmodified outer surface layer 126 and wires 131a, b are diffusion bonded to each other and have substantially similar chemical compositions, they also have the same level of corrosion resistance and/or biocompatibility; therefore, neither wire 131a nor wire 131b is a source for pinhole creation or a subsequent source of corrosion. It should, of course, be understood that wire 131a or 131b also can be clipped after the part is coated and a hook is no longer needed for part suspension.

[0031] In alternative embodiments, wire 131a or 131b can be threaded through a through hole (not shown) in core part 104 to provide a loop for suspending or supporting the part in the reactor. In a further embodiment, the part may simply be supported on the tips of wires 131a, b (not shown in FIG. 1 or 2) or on the tips of narrow objects like cylinders or rods and/or sharp pointed objects with a small end tip radius, such as cones or pyramids.

[0032] Using wires 131a, b to support the part creates a fully bonded and undistinguishable material interface for the wire. It should be understood that wires 131a, b are optional and may not be needed, for example if an alternative means for suspending the part in the reactor is provided and/or if the part is coated twice but supported at different locations each time.

[0033] In embodiments, object 100 can be a medical implant part, e.g. a screw or bracket made from a titanium grade 2 or grade 5 material.

[0034] FIG. 2 shows another illustrative embodiment of a partially coated object in accordance with the present disclosure. In this embodiment, the object is a top sealable chemical reactor vessel 210 made from a metallic composition and having a functional surface layer 202 that coats and thus protects at least a corrosion fluid and/or biomaterial contact area of vessel 210. In this embodiment, only the inside surface 203 of vessel 210 and the portion 206 of its flange 207 up to the sealing groove 209 constitute a corrosion fluid and/or biomaterial contact area. Since, in this case, the outside surface 211 of vessel 210 is not intended to be exposed to corrosive fluids, the corrosion resistance of outside surface 211 does not need to be enhanced with a conformal surface layer 202. Thus, the core part 204 can optionally be held on its outer surface 211 with a clamp 213 (or other mounting means known to those skilled in the art, like resting on a surface, holding by at least one screw, using a wire 231 of the same material composition as the surface layer 202, using a wire 231 of a different material composition from surface layer 202 whose

material is still process compatible with both the process for deposition of the carbon-based seed layer and the process for deposition of the functional surface layer). Wires 231a, b can be used to hang part 210 during a surface layer deposition process and then clipped (231b) as described above in connection with the embodiment of Fig. 1. As with the embodiment of Fig. 1, it should be understood that wires 231a, b are optional and may not be needed if an alternative means for suspending the part in the reactor is provided. Since wires 231a, b are not secured (e.g., welded) to part of the functional surface of vessel 210, the only requirement for the composition of wires 231a, b is that it survives a surface layer deposition process.

[0035] Functional surface layer 202 is separated into an unmodified layer 226 and a modified surface layer 222, marked by a transition surface 227. Core part 204 remains unmodified in this embodiment, and thus includes an unmodified core portion 228, but no modified core layer. In this embodiment, modified surface layer 222 alone forms an interface layer 220 that is in intimate and bonded contact with transition surface 227 and original outer surface 205 of core part 204.

[0036] FIG. 1 was shown with and FIG. 2 was shown without a modified core layer. However, it should be understood to the skilled in the arts that both a fully or partially coated object may or may not have a modified core layer.

[0037] As the functional surface layer 202 is deposited, interface layer 220 is simultaneously created due to the high temperature process requirements needed for economically depositing a functional surface layer of a suitable thickness and with substantially no pinholes. In embodiments, a dense (i.e. non-porous) gradient diffusion bond layer may form in the modified layer 222 of the functional surface layer with a gradient concentration transition of the material of the surface layer from high (close to about 90%) near the transition surface 227, to low (less than about 10%) near the interface between the modified surface layer 222 and the original outer surface 205 of part 204. At least one secondary gradient material component of the diffusion bond layer may be provided from the core part 204, such that the secondary gradient material is highly concentrated near the original outer surface 205 and at a low concentration (less than about 10%) near transition surface 227.

[0038] In embodiments, the interface layer may be at least about 1.3 times thinner in objects made by the present processes that include applying a carbon-based seed layer compared to objects made

where no carbon-based seed layer is employed. In embodiments, the interface layer may be from about 1.3 times to about 10 times thinner in objects made by the present processes that include applying a carbon-based seed layer compared to objects made where no carbon-based seed layer is employed. In embodiments, the interface layer may be from about 2 times to about 10 times thinner in objects made by the present processes that include applying a carbon-based seed layer compared to objects made where no carbon-based seed layer is employed. In embodiments, the interface layer may be from about 3 times to about 8 times thinner in objects made by the present processes that include applying a carbon-based seed layer compared to objects made where no carbon-based seed layer is employed. In embodiments, the interface layer may be from about 4 times to about 6 times thinner in objects made by the present processes that include applying a carbon-based seed layer compared to objects made where no carbon-based seed layer is employed.

[0039] The core part may be any, at least partially, metallic item for which it is desired to improve at least one aspect of its functionality (e.g., corrosion resistance, biocompatibility, etc.), either over all, or over a portion of the part. At least a portion of the core part can be made of any metallic composition that may benefit from the diffusion-reducing processes described herein. In embodiments, the core part may be made at least in part from any composition from which metal atoms will diffuse into the composition from which the selected functional surface layer is made if applied directly to the metallic core part.

[0040] In embodiments, the core part is made at least in part from a composition containing carbon, aluminum, cadmium, chromium, cobalt, copper, iron, lead, molybdenum, nickel, titanium, tungsten, zinc, or alloys containing one or more of these metals. In embodiments, the core part is made of a stainless steel. The core part may be made at least in part from a single metal or a combination of metals. Where made from a combination of metals, the core part may have different areas made from different metal compositions (e.g., layers, coatings, zones, brazing sections, etc.) or may be made from a uniform alloy composition. In embodiments, the material from which the core part is made does not include carbon.

[0041] In embodiments, the core part is made at least in part from a composition containing nickel (Ni). In embodiments, the core part may be made at least in part from pure Ni, or from an alloy containing Ni. In embodiments, Ni constitutes greater than about 15% by weight composition from

which the portion of the core part to be treated is made. In embodiments, the core part is made at least in part from a Ni-alloy containing at least about 40% Ni by weight. In embodiments, the core part is made at least in part from a Ni-alloy containing from about 40% Ni to about 70% Ni by weight. In embodiments, the core part is made at least in part from a Ni- alloy containing from about 50% Ni to about 60% Ni by weight. In embodiments, the metallic core material includes a Ni-alloy containing chromium, molybdenum, and greater than about 40% Ni by weight. In embodiments, the metallic core material includes a Ni-alloy containing chromium, molybdenum, and from about 50% Ni to about 60% Ni by weight. Alloys which may benefit from the presently disclosed processes include, but are not limited to: the HASTELLOY[®] alloys (commercially available from Haynes International, Inc., Kokomo, Indiana, USA); stainless steels reported as having 15% or greater Ni, such as Alloy 20, SUS310S, SUS317J1, SUS836L, and SUS890L; INCONEL[®] austenitic nickel-chromium-based superalloys; and MONEL[®] nickel alloys. Practically pure nickel may also exhibit some benefits from the presently disclosed processes.

[0042] In embodiments, the core part may be any Ti-containing metallic item for which it is desired to improve at least one aspect of its functionality (e.g., corrosion resistance, biocompatibility, etc.), either over all, or over a portion of the part. At least a portion of the core part can be made of any titanium-containing composition that may benefit from the processes described herein. In embodiments, the core part may be made at least in part from pure Ti, or from an alloy containing Ti. In embodiments, Ti constitutes greater than about 15% by weight composition from which the portion of the core part to be treated is made. In embodiments, the core part is made at least in part from a Ti-alloy containing at least about 40% Ti by weight. In embodiments, the metallic core material includes a Ti-alloy containing at least about 80% Ti by weight. In embodiments, the metallic core material is from about 90% Ti to about 100% Ti by weight. Alloys which may benefit from the presently disclosed processes include, but are not limited to: titanium grade 1, 2, 5, 9, 12, or 23; Alpha alloys such as Ti-5Al-2Sn-ELI or Ti-8Al-1Mo-1V; near-alpha alloys such as Ti-6Al-2Sn-4Zr-2Mo, Ti-5Al-5Sn-2Zr-2Mo, IMI 685 or Ti 1100; alpha and beta alloys, such as Ti-6Al-4V, Ti-6Al-4V-ELI or Ti-6Al-6V-2Sn; and beta and near beta alloys, such as Ti-10V-2Fe-3Al, Ti-29Nb-13Ta-4.6Zr,[3] Ti-13V-11Cr-3Al, Ti-8Mo-8V-2Fe-3Al, Beta C or Ti-15-3. Practically pure titanium may also exhibit some benefits from the presently disclosed processes.

[0043] The core part may have any desired shape. In embodiments, the core part may have a generally uniform surface (e.g., flat sheet, sphere, etc.), simple geometries (e.g., axially symmetric geometries), or complex-part geometries (e.g., geometries with intricate features, such as different surface height steps, sharp corners, inside and outside corners, dead end pockets, deep recessed holes, threaded blind holes, etc., which are typically seen in parts used for industrial applications). Applying a functional surface coating onto core parts with more complex surface geometries in a cost-efficient manner is typically accomplished through the use of non-line-of-site deposition processes, such as a CVD process.

[0044] To prepare the core part for coating with a functional surface layer, a carbon-based seed layer is applied to at least a portion of the core part. In embodiments, the carbon-based seed layer applied to the core material is of the composition C_xM_y , where M can be any element or combination of elements, where the atomic percent is defined as $x/(x+y)*100$. The term “carbon-based” as used herein with respect to any layer means that at the time the layer is deposited, it contains at least about 50% atomic percent carbon. In embodiments, the carbon-based seed layer applied to the core part contains at least about 90% atomic percent carbon. In embodiments, the carbon-based seed layer has a thickness of from about 50 nm to about 5,000 nm. In embodiments, the carbon-based seed layer has a thickness of from about 100 nm to about 2,000 nm. In embodiments, the carbon-based seed layer is applied at a thickness of from about 200 nm to about 500 nm. As those skilled in the art will appreciate, core parts with different material compositions may obtain a different seed layer thickness despite undergoing the same carbon seed layer deposition process. Thus, the composition, thickness and deposition conditions for the carbon-based seed layer may be optimized for any given core material to be treated and for a chosen surface layer deposition process.

[0045] In embodiments, the seed layer may include a combination of the elements of carbon, nitrogen and/or metal, either in a multilayer format (binary, tertiary, etc.) and/or a co-deposited gradient film format or a single layer made from a single carbon material format. In particular, a nitrogen enrichment, nitrating or co-nitrating process can be done utilizing either simultaneously or afterward utilizing ammonia (NH_3 or N_2) and/or H_2 in the 800-1,000 °C range to nitrate a core material and/or to cause a nitrating reaction with a co-depositing carbon and/or metal film (for example, a Ti_xC_y , Ti_xN_y , or $Ti_xC_yN_z$ film). In particular, metal films that can be deposited or co-

deposited in a gas phase reaction inside a CVD reactor, like H₂ reduction of metal chlorides at similar or lower process temperatures than the surface layer deposition process are desired, such as TiCl₄, FeCl₃, NiCl₂, MoCl₅, CoCl₂, etc., as well as CVD metal film deposition from metal-carbonyl precursors, like Ni(CO)₄, Fe(CO)₅, Mo(CO)₆, Cr(CO)₆, etc., and/or carbide and/or nitrite, and/or carbide and nitrate metal forming films from metal-organics precursors.

[0046] Without wishing to be bound to any theory, it appears that the controlled deposition of a carbon-based seed layer onto the core part prior to the application of a functional surface layer may influence the width of the interface layer and/or the porosity of at least one of its sublayers, for example the modified core layer 124. For parts that exhibit a Kirkendall porosity layer after undergoing a surface layer deposition without an intervening carbon-based seed layer deposition, the application of the carbon-based seed layer prior to the surface layer deposition may reduce and/or eliminate the formation of such a Kirkendall porosity layer by forming an effective diffusion barrier near the outer surface of the core part for a range of metallic materials, such as a nickel diffusion barrier. In embodiments, the modified layer of the core part is substantially void of a Kirkendall porosity layer, wherein “substantially void” means that the thickness of any Kirkendall porosity layer present is less than about 2 μm. Applying the carbon-based seed layer may enable more control over the thickness, ductility, and/or other qualities of the interface layer, may enable improved adherence of a functional surface layer to the core part for a range of metallic materials, and/or may improve the corrosion resistance and/or biocompatibility of the interface layer 120 or 220. Applying a carbon-based seed layer may enable in some circumstances the manufacture of objects for industrial, medical (for example, improving biocompatibility of biological implants), or other corrosive applications having improved corrosion-resistance and/or biocompatibility, an extended use lifetime, and/or a slower corrosion rate in case of a surface layer penetration event. In addition, deposition of a carbon-based seed layer onto the core part prior to the application of a functional surface layer may enhance mechanical attachment (bonding) of the core material (e.g., a Ni or Ni-alloy core material or Ti or Ti-alloy core material) and mechanical performance of the surface layer by forming a suitable interface layer between the surface layer and the core material that includes a suitable diffusion bond layer at its top layer (i.e. a layer that is in material contact with the surface layer) and by improving the adhesion and mechanical strength of all the layers of the interface layer. The addition of the carbon-based seed layer may also affect the surface roughness of the surface layer; for example, it may lead to a functional

surface layer having a less or more dendritic structure because of the carbon-based seed layer. For example, a decrease in the roughness of the surface layer may allow the surface to become more sealable. Alternatively, an increase in surface roughness and/or surface porosity in the outermost surface region of the surface layer may make such a surface more biocompatible. Applying the carbon-based seed layer may have other functional benefits, such as improving biocompatibility; changing hardness; changing electrical and/or thermal conductivity; or facilitating bonding to subsequent coatings such as, for example, thermal spray coatings that improve the wear resistance of the corrosion protective surface layer. By further overcoating the functionally coated object with a thermal spray layer having desired mechanical abrasion resistant properties and no deleterious effect in the corrosion resistance of the underlying functional surface coating, the object's corrosion resistance and/or other properties may further improve for industrial process applications.

[0047] In embodiments, to apply the carbon-based seed layer, the core part first undergoes a cleaning procedure. After cleaning the core part, the carbon-based seed layer may be applied to the core part using any technique known in the art. In embodiments, the cleaned core part is placed inside a CVD reactor configured for carbon nanotube growth. Suitable reactors include, for example, any appropriately configured FIRSTNANO™ EASYTUBE® horizontal tube furnace CVD systems (sold by CVD Equipment Corporation, Central Islip, NY, USA). Generally, the use of such systems involves heating up the core part to a temperature in the range of 500 to 1,000 °C inside a sealed process chamber (for example, made from quartz) and then annealing under H₂ gas flow for 5 to 60 minutes to remove any impurities, surface oxide layers and surface carbons/oils from machining and handling of the core part and, when multiple core parts are being treated simultaneously, to allow all parts to reach the same temperature before starting the annealing step, H₂ reduction, and/or seed layer deposition process step. Then a hydrocarbon gas (e.g., ethylene, acetylene, methane, propane, natural gas, etc.) is added to H₂ together with argon for an appropriate period of time (typically 1 to 60 minutes) to enable a carbon seed layer formation over the core material. Thereafter the process gas is switched to argon or another suitable inert gas during a cooling down period, after which the parts having a carbon-based seed layer may be unloaded from the reactor or left within the reactor for deposition of the functional layer. It should be understood that the particular settings/conditions for operating the CVD system may be

controlled based on the composition of the core part to provide a carbon-based seed layer of a desired thickness on the part.

[0048] Other contemplated methods for forming the carbon-based seed layer include, but are not limited to, spraying, dipping, electrostatic CVD, plasma assisted CVD, thermal evaporation, e-beam evaporation, sputtering or any other suitable deposition process that allows first a sufficient conformal deposition of a polymer coating onto the outer surface a core material and subsequently the conversion of the polymer film into a carbon film. To convert the polymer film to a carbon film, the polymer coated part is placed inside an atmospherically sealed oven that is purged and filled with suitable process gases (for example H₂ and/or one or more inert gases) and then heat ramped in such a way that the polymer film is converted into a carbon film, as known to the skilled in the art. Alternatively, the carbon-based seed layer may be formed by depositing a fine dispersed film of ultra-fine carbon particles (for example carbon black) with/or without a temporary binder. An alternative method of applying a carbon-based seed layer includes first the dipping, spraying, soaking, or painting of a part outside surface with a precursor resin used for carbon fiber manufacturing and/or carbon to carbon bond creation, and then the subsequent conversion of the precursor into a dense carbon layer by appropriately heating up the precursor- coated part inside an oxygen free oven under a reducing atmosphere.

[0049] Once the carbon-based seed layer is applied to the core part, the functional surface layer may be applied. In embodiments, the functional surface layer includes a refractory metal. In embodiments, the refractory metal constitutes greater than about 80% of the unmodified portion of the functional surface layer by weight. In embodiments, the refractory metal is tantalum (Ta). In embodiments, tantalum constitutes greater than about 80% of the unmodified portion of the functional surface layer by weight. In embodiments, the functional surface layer is made from a tantalum alloy that contains greater than about 95% tantalum. In embodiments, the functional surface layer includes a metal selected from tantalum (Ta), niobium (Nb), molybdenum (Mo), tungsten (W), titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (Va), chromium (Cr), ruthenium (Ru), rhenium (Rh), osmium (Os), iridium (Ir), platinum (Pt), or an alloy containing one or more of these metals. In embodiments, the unmodified portion of the functional surface layer includes an alloy containing at least about 10% by weight of one or more of tantalum (Ta), niobium (Nb), molybdenum (Mo), tungsten (W), titanium (Ti), zirconium (Zr), hafnium (Hf),

vanadium (Va), chromium (Cr), ruthenium (Ru), rhenium (Rh), osmium (Os), iridium (Ir), or platinum (Pt). The thickness of the deposited functional surface layer may, in embodiments, be from about 10 μm to about 200 μm , and, in embodiments, from about 20 μm to about 50 μm , in order to provide a notable extended usage-lifetime in a corrosive environment and/or biological environment (for example, implants) and to allow the object to survive wear and tear during normal usage and/or installations in its intended environment.

[0050] The application of the functional surface layer can be done via any suitable method within the purview of those skilled in the art. Such deposition methods include CVD H_2 reduction of a refractory metal chloride (such as TaCl_5 , NbCl_5 , etc.) or salt bath electrolytic deposition, typically at temperatures greater than about 700 $^\circ\text{C}$, in embodiments greater than 800 $^\circ\text{C}$. The lower the process temperature of such a surface layer deposition process, and the shorter the duration a core part is exposed to elevated temperatures, the less changes occur to any of the material properties of the core part (for example, strength, ductility, fatigue strength, crack propagation, etc.). Application of the functional surface layer may be done in the same reactor, or the carbon seed layer-coated part may be moved to a different reactor.

[0051] In embodiments, the functional surface layer is substantially pinhole free. The presence of pinholes can be tested using an accelerated corrosion test consisting of a 48-hour immersion of the surface coated part in a 25% hydrochloric acid bath at 70-75 $^\circ\text{C}$. The term “substantially pinhole free” as used herein means a functional surface layer coated object passed the above described accelerated corrosion test without visible pinholes thereafter on the surface area of the coated object part that has been corrosion tested.

[0052] A “failure” as used herein with respect to a layer means the occurrence and/or formation of a local delamination zone as evidenced by a bubbling up of the surface coating layer above its reference surface as observable with a naked eye, indicating a local debonding region. Though not wishing to be bound by any size restriction, in general, a 1-10 mm-sized bubbling up of a layer may be observed with the naked eye. The probability of such a failure may correlate to the concentration of a material in the core material that diffuses into the functional surface layer.

[0053] FIG. 3 outlines illustrative methods for manufacturing a functionally coated object in accordance with the present disclosure. In step 300, a core part is manufactured. The core part may

be formed into a desired shape using any technique within the purview of those skilled in the art. Suitable techniques include, for example, molding, casting, pressing, stamping, etching, machining, welding, brazing, and the like. When manufacturing the core part, any sharp edges should be de-burred since burrs can weaken or puncture subsequently applied layers, resulting in local pinholes or other defects in those layers.

[0054] In step 302, the core part is cleaned. Cleaning removes, for example, oil residues left over from machining the core part and/or removes scale and/or surface oxides. Cleaning may be accomplished through methods including, but not limited to, standard metal surface degreasing; one or more baths at room temperature and/or heated, with and/or without ultrasonic and/or liquid recirculation systems, including alkaline, acid, electropolishing, rinsing, and/or pickling bath.

[0055] During the optional step 304, at least one wire (for example, a tantalum or stainless-steel wire), is spot welded or otherwise secured onto the core part. Securing the wire should occur at a non-critical and non-functional location of the cleaned core part or, at minimum, in one of its least critical and least-functional locations. The wire can subsequently be used for mounting the core part, for example, either by attaching the loose end of a wire to another hanging wire and/or a wire clamp, by hanging the wire from a loop formed from the wire, or by wrapping the wire around a support bar or beam or equivalent fixtures. For example, the wire could be attached to the side of the non-sealing portion of a flange and/or outside of a vessel and/or tubular part into which a corrosive fluid will flow during the intended utilization of the part. It should be understood that step 304 can be done prior to the carbon deposition or after the carbon deposition step 308. Securing more than one wire, for example, three wires, to the core part might be employed for a heavier core part and/or to assure its proper orientation inside a process reactor. Process step 304, if used at all, may be performed before a cleaned part is loaded into a surface layer deposition system, i.e. before step 310. In embodiments, step 304 is completed before step 306. If step 304 is done after step 308, the carbon seed layer might get locally damaged (oxidized away), causing the attachment region of the wire and its surrounding area to be a potential weak spot in the corrosion protection of the part. For parts such as vessel 210 (see Fig. 2) having areas that are not subjected to a corrosive environment, the composition of the wire and the timing of process step 304, if used at all and if the wire is located outside the area expected to be subjected to a corrosive

environment during use, are less likely to impact the integrity of the functional surface layer in the area that is expected to be subjected to a corrosive environment.

[0056] Before a core part can be coated with a seed layer in step 308, it is loaded into a suitable carbon seed layer deposition system, as in step 306. During the loading step 306, each core part may be hung from or otherwise supported by at least one wire (e.g., as described above with respect to wires 131a, b, of Fig. 1) so that all of the core part outer surface can be evenly exposed to the carbon film-producing source or, at a minimum, the portion of the core part outer surface that is critical for a specific application of the part in a partially corrosive environment (for example, the inside of a reactor vessel) can be evenly exposed to the carbon film producing source. On the other hand, when using a CVD carbon seed layer system, even inch-sized square parts sitting on a frosted quartz plate get sufficient exposure to the respective carbon film generating precursor gases, such that the bottom and top side of such primitively mounted core parts still achieve an interface layer as described hereinabove and hereinbelow, when later coated with the functional surface layer.

[0057] It should be understood that in other embodiments, the core part may be supported or mounted within the reactor by other means known to those skilled in the art, such as by the use of a mounting fixture or other holder or hung by a not spot-welded wire or rod. However, such other means can cause a “blind spot” on any holder contact area; thus, when the coated part is removed from the mounting fixture, the surface area of core object 104 that was in contact with the mounting fixture may not be coated. As another example, core object 104 can be supported on sharp pins of a different material than surface layer 102 and/or thicker pins of the same material as surface layer 102 that are not easily clippable after a respective surface layer coating process step without damaging the surface layer 102. If a blind spot is formed or a surface layer perforation is detected after removing part 100 from the mounting fixture, then re-mounting the part using a different fixture (or the same fixture, but installing the part in a different orientation) to expose any blind spot, and subsequently performing a second surface layer deposition run can also yield a fully sealed object 100, however likely at a higher production cost.

[0058] After the core part is loaded inside a carbon seed layer deposition system, a carbon seed layer is deposited during step 308. It should be understood that an atmospheric CVD, sub-atmospheric or higher than atmospheric processing conditions may be employed to apply the

carbon-based seed layer, with respective adjustment in flow rates and/or processing time, as known to those skilled in the art. In embodiments, the carbon seed layer is formed over all corrosive fluid and/or biomaterial contact areas of the core part.

[0059] If the carbon seed layer deposition system and the surface layer deposition system are two different systems, as in certain embodiments in accordance with this disclosure, then the optional step 310, transferring and mounting the carbon seed layer-coated parts to the surface layer deposition system is performed. Again, the carbon seed layer coated parts need to be mounted in the surface layer deposition system which can be done using one of the techniques previously described or any other technique within the purview of one skilled in the art. If, as in certain embodiments, both the carbon seed layer deposition system and the surface layer deposition system are identical, those skilled in the art will appreciate that step 310 is not needed.

[0060] It should be understood that the present methods may be used to simultaneously apply a functional surface layer in a single batch run onto parts having different shapes, compositions, or both. It should be further understood that not all parts in the batch run need to have a carbon-based seed layer pre-applied thereto; rather, some parts included in the batch run may be treated without application of a carbon-based seed layer.

[0061] The application of the functional surface layer, step 312, can be done via methods within the purview of one skilled in the art, such as CVD H_2 reduction of a refractory metal chloride, or salt bath electrolytic deposition as described above.

[0062] Once the functional surface layer is deposited in step 312, the object is removed from the surface layer deposition system at step 314, and any wires (e.g., used for suspension or support of the part in the reactor(s)) may optionally be trimmed or removed from the object in step 316.

[0063] In embodiments, the thickness of the interface layer in objects made by the present processes (that include applying a carbon-based seed layer) may be thinner compared to objects made where no carbon-based seed layer is employed. In embodiments, the interface layer in objects made by the present processes may be more ductile and/or present improved adhesive qualities compared to objects made where no carbon-based seed layer is employed. In embodiments, the porosity of any of the sublayers of the interface layer may be reduced and/or practically eliminated

and/or the functionality (e.g., corrosion resistance, biocompatibility, etc.) of the interface layer may be improved.

[0064] In embodiments, the interface layer produced in accordance with the present processes has a thickness of less than about 10 μm , in embodiments in the range of about 0.5 μm to about 10 μm , in other embodiments in the range of about 0.5 μm to about 5 μm , in other embodiments in the range of about 0.7 μm to about 2 μm , and in further embodiments in the range of about 0.7 μm to about 1.5 μm . The addition of the carbon-based seed layer may impact the thickness of the interface layer, minimize interface layer brittleness, and/or reduce local adhesion failures of the local bonding of the surface layer to the core part, which can result in “bubbled-up” de-bonded regions when the object is exposed to mechanical stress during installation and/or usage. For example, thermal shock/thermal expansion stress during usage of an object or during the process steps 308 or 312, can lead to premature pinhole creation due to the creation of a fatigue tear from mechanical flexing of a de-bonded surface layer over time when such a de-bonded region of the surface layer gets exposed to turbulence. Through such “cracks and/or pinholes,” a corrosive fluid has access to the underlying interface layer and/or the unmodified portion of the core part thus shortening the usage lifetime of the object.

EXAMPLES

EXAMPLE 1 – Tantalum Deposited on a Carbon-Coated HASTELLOY[®] Core Part

[0065] A HASTELLOY[®] C-276 part is cleaned in an ultrasonic bath in acetone and alcohol and then has been placed inside an EASYTUBE[®] 2000 CVD reactor (commercially available from CVD Equipment Corporation, Central Islip, NY) configured for carbon nanotube growth and having a process tube with a 3” inner diameter.

[0066] The seed layer is deposited by first heating the part up to 825 °C and then annealing for 30 minutes under H₂ gas flow to remove any impurities, surface oxide layers and surface carbons/oils. After the loaded part reaches the desired temperature, C₂H₄ (ethylene) gas is added to H₂ together with argon (Ar) to create a respective flow (1.75 SLPM of Ar, 0.25 SLPM of H₂ and 0.1 SLPM of C₂H₄) for a growth time of 30 minutes to enable a carbon seed layer formation over the core part. Thereafter the process gas is switched to 2.9 SLPM of Ar during cooling down to 200 °C,

after which the part is unloaded from the reactor. When cross sectioned and inspected with an SEM, the part was shown to have a carbon layer coating ranging from about 100 nm to about 300 nm, depending on the portion of the part observed. Optional other gases such as N_2 , NH_3 , metal organics, $TiCl_4$, etc. may be co-introduced in the 50-1,000 sccm range with the C_2H_4 to form a binary and/or tertiary carbon-based seed layer. (FIG. 4 and 5 utilize only C_2H_4 , H_2 and Ar during the carbon seed layer deposition process).

[0067] A functional surface layer is applied to the carbon-coated part using a TANTALINE[®] treatment (a tantalum chemical vapor coating technology commercially available from Tantaline CVD ApS), that is based on a hydrogen reduction of tantalum pentachloride. An SEM image of a cross section of the resulting object (after a metallurgical sample preparation process) is shown in FIG. 4. As seen in Fig. 4, interface layer 20 includes three sublayers (22a, 22b, and 22c). Together they form a diffusion bond layer 22 at the bottom part of surface layer 12. There is basically no (visible) Kirkendall porosity layer 24 at the top part of core material 14. The deposited surface layer 12 is visually separable into a top, unmodified portion 26 of surface layer 12 and a bottom, modified portion of surface layer 12, i.e. diffusion bond layer 22. The core material 14 is not visually separable into a top, modified portion of core material 14, i.e. Kirkendall porosity layer 24 and a bottom, unmodified portion 28 of core material 14. The total thickness of the interface layer 20 is 2.4 μm . Small grain pullouts 39 caused by the preparation of the part for SEM analysis are visible in the SEM image.

[0068] The white arrow in Fig. 4 marks the spatial location for the EDX line scan shown in Fig. 5. The line scan in Fig. 5 depicts the three major layers of the carbon-coated part: the unmodified surface portion 26, the interface layer 20, and the unmodified core portion 28. The unmodified surface portion 26 and the interface layer 20 are separated by the inner transition surface 27 of the surface layer 12 at -2.4 μm . The unmodified core portion 28 and the interface layer 20 are separated by the original surface layer 5 of the core part 14 at 0 μm . The interface layer 20 can be further divided into three sub-layers or regions. From -2.4 μm to -1.6 μm , labeled as region or sublayer 22a, basically only the tantalum decays. From -1.6 μm to -0.63 μm , labeled as region 22b, the tantalum levels dip and then rise back up, while the carbon concentration reaches its peak concentration at the end of this region 22b. Finally, region 22c, from -0.63 μm to 0 μm , tantalum levels drop significantly, quickly approaching close to 0% concentration, and at the same time the

carbon concentration level decays with some possible noise related amplitude oscillations superimposed and the Ni concentration raises from close to zero to the C-276 bulk level. The carbon enriched regions 22b and 22c together are approximately 3-6 times thicker than the approximately 300-500 nm thickness of the original carbon seed layer deposited on the core part prior to the tantalum surface layer deposition, suggesting some occurrence of diffusion of the carbon seed layer into the tantalum deposited surface layer during the surface layer deposition process done at elevated process temperatures. The diffusion of the carbon and the tantalum together in region 22c seems to have essentially stopped further nickel diffusion into any of the other the tantalum sublayers (26, 22a and 22b), as can be seen around -0.63 μm mark and further along the negative axis, where the nickel concentration is close to 0% (i.e., within the detection limit of the used EDX system). The line scans of Fig. 5 depict changes in material concentration that are not always also detectable by eye in the SEM image (which is primarily sensitive to electrical conductivity changes and, to a lesser degree, to material composition changes) of Fig. 4, specifically in region 22a and the beginning of region 22b, so more sensitive analytical methods have to be used, like a line scanning EDX system, for example.

COMPARATIVE EXAMPLE A – Tantalum on an Un-Coated HASTELLOY® Core Part

[0069] A functional surface layer is applied directly to a HASTELLOY® C-276 part (previously cleaned in an ultrasonic bath in acetone and alcohol) using a TANTALINE® treatment, a tantalum chemical vapor coating technology commercially available from Tantaline CVD ApS. An SEM image of a cross section of the resulting object is shown in FIG. 6. As seen in Fig. 6, interface layer 20 includes two distinguishable sublayers: a diffusion bond layer 22 at the bottom part of surface layer 12; and a Kirkendall porosity layer 24 located at the top part of core material 14. The deposited surface layer 12 is visually separable into a top, unmodified portion 26 of surface layer 12 and a bottom, modified portion 22 of surface layer 12, i.e. diffusion bond layer 22, which includes sublayers 22a, 22b, and 22c. Similarly, core material 14 is visually separable into a top, modified portion 24 of core material 14, i.e. also called herein a Kirkendall porosity layer 24, and a bottom, unmodified portion 28 of core material 14. The total thickness of the interface layer 20 is 12 μm . Small grain pullouts 39 caused by the preparation of the part for SEM analysis are visible in the SEM image.

[0070] The white arrow in Fig. 6 marks the spatial location for the EDX line scan shown in Fig. 7. The line scan in Fig. 7 depicts the four major layers of the non-carbon-coated part: the unmodified surface portion 26, the modified surface layer 22, the modified core layer 24, and the unmodified core portion 28. Together, the modified surface layer 22 and the modified core layer 24 form the interface layer 20. The unmodified surface portion 26 and the modified surface layer 22 are separated by the inner transition surface 27 of the surface layer 12 at $-5\text{ }\mu\text{m}$. The unmodified core portion 28 and the modified core layer 24 are separated by the inner transition surface 29 of the core part 14 at $7\text{ }\mu\text{m}$. Further, the modified core layer 24 and the modified surface layer 22 are separated by the original surface 5 of the core part 14 at $0\text{ }\mu\text{m}$. The modified surface layer 22 can be further divided into three regions. From $-5\text{ }\mu\text{m}$ to $-3.6\text{ }\mu\text{m}$, labeled as region 22a, the tantalum concentration reduces from approximately 100-90% to approximately 40% and the Ni concentration raises from close to zero (within the EDX detection limit) to about 42%. From $-3.6\text{ }\mu\text{m}$ to $-1.1\text{ }\mu\text{m}$, labeled as region 22b, both the tantalum and nickel levels remain relatively stable. Finally, region 22c, from $-1.1\text{ }\mu\text{m}$ to $0\text{ }\mu\text{m}$, the tantalum and nickel levels drop, with tantalum levels dropping below approximately 5% and nickel levels dropping below approximately 15% (all within EDX detection limit) and Cr and Mo raising from a minimum detection level to their approximate concentrations in the unmodified core portion 28.

[0071] In the modified core layer 24, from $0\text{ }\mu\text{m}$ to $7\text{ }\mu\text{m}$, the nickel concentration initially fluctuates between 15% and 25% and then towards the end raises to the nickel concentration of the unmodified core portion 28, i.e. about 40%, and, thus, can alternatively be referred to as the nickel depletion and/or Kirkendall porosity region or sublayer. This region is likely the source of the majority of the nickel that enters the modified surface layer 22, and can be found in particular in sublayer 22b. Chromium and molybdenum levels remain relatively constant in the modified core layer 24 and are close to their concentration level in the unmodified core portion 28. In the unmodified core portion 28, the nickel concentration stays at to approximately 40%; therefore, this portion has likely lost relatively little, if any, nickel. The excessive nickel diffusion from the modified core portion 24 into the modified surface portion 22, especially sublayer 22b, forms the Kirkendall porosity layer which contains numerous grain boundaries 36 and voids 38, as visible Fig. 6. The line scans of Fig. 7 depict changes in material concentration that are not visually detectable in the SEM image of Fig. 6, specifically in region 22a.

[0072] A comparison of Figs. 4 and 6 shows that the interface layer 20 in the sample of Example 1 prepared in accordance with the present disclosure by first applying a carbon-based seed layer is $(12)/(2.4) = 5\times$ thinner than the interface layer 20 in the sample prepared in the Comparative Example A in a conventional manner (i.e., without first applying a carbon-based seed layer). In addition, the Kirkendall porosity layer 24, that is very visible in FIG. 6 for Comparative Example A, is virtually eliminated in FIG. 4 for the sample of Example 1 prepared in accordance with the present disclosure, i.e. with a carbon-based seed layer being applied before the surface layer deposition process step.

[0073] Ni has a particularly high diffusion rate under the conditions traditionally used for a refractory metal surface layer deposition process. This is particularly true when the refractory metal is at least mostly Ta-based. In particular, for Ni-alloys with high Ni-concentration (for example, 50-60% as in HASTELLOY® C-276), prior art object manufacturing methods lead to the formation of a significant Kirkendall porosity layer 24 at the location of a modified core layer of the core part. The thicker and more porous such a Kirkendall porosity layer 24, the weaker the adhesion between the functional surface layer and the core part and the weaker the corrosion resistance of the interface layer after a pinhole punctures through the unmodified portion of the Ta-based functional surface layer.

[0074] An interface layer corrosion surface layer penetration test was performed by first drilling a 1 mm hole through the Ta surface layer about 1-2 mm deep into the HASTELLOY® C-276 core material and then putting the surface penetrated objects through a standard accelerated corrosion test. As a result, for a comparative sample as shown in FIG. 6, 3-10 mm large bubbles formed on the Ta surface layer over a 10-12mm wide zone while no bubbles formed for a sample including the carbon-based seed layer, as shown in FIG. 4. Under test conditions, this corrosive acid was able to corrode at least one sublayer of the interface layer (presumably the Ni-depletion layer) sideways over at least >10 -100 times larger area than the area of the intentionally made surface penetration for a comparative sample as shown in FIG. 6, thus showing that at least one sublayer of the interface layer for the comparative sample is not very corrosion resistant. The HASTELLOY® C-276 core material sample still looked unaltered at the end of this test phase,

indicating that after a full surface layer penetration the corrosion resistance of the interface layer 20 of such a treated HASTELLOY® C-276 core material sample was superior to the comparative sample.

[0075] As can be seen from FIG. 6 and 7, the Ni departs primarily from the boundaries of the C-276 grains 36 and thus creates voids 38 between them, leaving behind a more loosely connected and porous grain structure. This porous grain structure, forming the Kirkendall porosity layer 24 which in the case shown in FIG. 6 is so thick (7 μm) that multiple small grains 36 are stacked on top of each other that are only partially connected with each other, is mechanically much weaker than any of the other fully dense layers, thus making it the weakest link for the adherence of surface layer 12 to unmodified core material 28. Such a mechanically weaker Kirkendall porosity layer 24 is more likely to mechanically fail when exposed to tensile stress or mechanical stress. Tensile stress between diffusion bond layer 22 and unmodified core material 28, for example, can occur due to flexing a respective object during use and/or installation. Alternatively, mechanical failure may occur due to thermal differential expansion stress caused by a slow or fast temperature change of the object and the different thermal expansion rates of the different materials of which each layer or core material is comprised of. For example, such thermal differential expansion stress may occur due to cooling the objects after a high temperature Ta surface layer deposition process and/or due to repetitive small thermal shocks of such an object or part of such an object over time, thus weakening the adhesion between the top and bottom surface of Kirkendall porosity layer 24. It should be noted that the small grain pullouts 39 visible in both FIG. 4 and FIG. 6 are present due to the preparation methods of the samples and are not equivalent to the voids 38 visible in FIG. 6.

[0076] In addition, the removal of Ni from the alloy grains 36 inside Kirkendall porosity layer 24 with the highest removal rate near the grain boundaries of grains 36 results in a different (Ni depleted) stoichiometric composition for grains 36 than that of the unmodified portion of the core material 28. In the event of a penetration of the surface layer 12 down to the Kirkendall porosity layer 24, the porosity between grains 36 caused by the grain boundary voids 38 allows any corrosive liquids that reach the Kirkendall porosity layer to spread much faster throughout the Kirkendall porosity layer 24 and quickly contact many grains simultaneously. In addition, since a significant portion of the surface area of partially isolated grains 36 is now exposed due to inter-grain voids 38, such exposure of the Kirkendall porosity layer 24 to a corrosive liquid results in a

faster lateral erosion rate of the Kirkendall porosity layer 24. Together, all of these factors ensure that Kirkendall porosity layer 24 is the least corrosion-resistant part of such a Ta surface-coated object. Therefore, over prolonged exposure to corrosive liquids, most of Kirkendall porosity layer 24 erodes before the unmodified portion of core material 28 or the surface layer 12. This then results in nearly all of the surface area of the unmodified core material getting simultaneously exposed to a corrosive liquid, thereby accelerating its corrosion rate.

[0077] FIG. 6 further indicates that the resulting thickness of the diffusion bond layer 22 is approximately 5 μm and that the resulting thickness of the Kirkendall porosity layer 24 is approximately 7 μm , resulting in a total thickness of approximately 12 μm for interface layer 20. Typically, the more such an interface layer thickness exceeds a threshold thickness of approximately 3-5 μm , the more brittle it becomes, and the more likely it fails an acid bath test after a bend test and the more likely local surface layer delamination failures are to occur during manufacture, installation, and/or utilization of such parts.

[0078] While several embodiments of the present functionally coated objects and methods have been shown in the drawings and described, it is not intended that the present disclosure be limited thereto, as it is intended that the disclosure be as broad in scope as the art will allow and that the specification be read likewise. It should be understood that the foregoing description is only illustrative of the present disclosure. Various alternatives and modifications can be devised by those skilled in the art without departing from the disclosure. Such modifications and variations are intended to be included within the scope of the present disclosure. In addition, the features illustrated or described in connection with one exemplary embodiment may be combined with the features of other embodiments. Therefore, the above description should not be construed as limiting, but merely as exemplifications of presently disclosed embodiments.

CLAIMS

1. A coated part comprising:
 - a core part including an unmodified portion and optionally a modified layer;
 - a functional surface layer including an unmodified portion and a modified layer in contact with a portion of the core part, the modified layer of the functional surface layer including a diffusion barrier layer; and
 - an interface layer defined by the modified layer of the functional surface layer and, where present, the modified layer of the core part.
2. The coated part of claim 1 wherein the modified layer of the core part, when present, is substantially void of a Kirkendall porosity sublayer.
3. The coated part of claim 1 wherein the interface layer has a thickness in the range of about 0.5 μm to about 10 μm .
4. The coated part of claim 1 wherein the core part is made at least in part from a composition that includes nickel (Ni).
5. The coated part of claim 1 wherein Ni constitutes greater than about 15% of the metallic core material by weight.
6. The coated part of claim 1 wherein the core part is made at least in part from a Ni-alloy containing at least about 40% Ni by weight.
7. The coated part of claim 1 wherein the core part is made at least in part from a Ni-alloy containing chromium, molybdenum, and greater than about 40% Ni by weight.
8. The coated part of claim 1 wherein the core part is made at least in part from a composition that includes titanium (Ti).
9. The coated part of claim 1 wherein the functional surface layer is made from a composition that includes a refractory metal.

10. The coated part of claim 9 wherein the refractory metal constitutes greater than about 80% of the unmodified portion of the functional surface layer by weight.
11. The coated part of claim 9 wherein the refractory metal is tantalum (Ta).
12. The coated part of claim 1 wherein the functional surface layer includes tantalum (Ta), niobium (Nb), molybdenum (Mo), tungsten (W), titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (Va), chromium (Cr), ruthenium (Ru), rhenium (Rh), osmium (Os), iridium (Ir), platinum (Pt), or an alloy of one or more of these metals.
13. The coated part of claim 1 wherein the unmodified portion of the functional surface layer includes an alloy containing at least about 10% by weight of one or more of tantalum (Ta), niobium (Nb), molybdenum (Mo), tungsten (W), titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (Va), chromium (Cr), ruthenium (Ru), rhenium (Rh), osmium (Os), iridium (Ir), platinum (Pt).
14. The coated part of claim 1 wherein the functional surface layer has a thickness of greater than about 10 μm .
15. The coated part of claim 1 wherein the functional surface layer is substantially pinhole free.
16. The coated part of claim 1 further comprising a wire secured to the core part.
17. The coated part of claim 1 wherein the interface layer is at least about 1.3 times thinner compared to the interface layer of an object made of the same composition core part and functional surface layer, but without a carbon-based seed layer.
18. A method for making functionally coated objects, the method comprising:
 - applying a carbon-based seed layer to coat at least a portion of a core part; and
 - depositing a functional surface layer on at least a portion of the carbon-coated portion of the core part.
19. The method of claim 18 further comprising cleaning the core part before applying the carbon-based seed layer.

20. The method of claim 18 further comprising mounting the core part in a reactor before applying the carbon-based seed layer.
21. The method of claim 20 wherein the core part includes a wire and mounting the core part in a reactor includes hanging the core part by the wire.
22. The method of claim 18 further comprising spot welding a wire to the core part.
23. The method of claim 22 further comprising removing at least a portion of the wire after deposition of the functional surface layer.
24. The method of claim 18 wherein the carbon-based seed layer is applied by chemical vapor deposition.
25. The method of claim 18 wherein the carbon-based seed layer is applied at a thickness of from about 50 nm to about 5,000 nm.
26. The method of claim 18 wherein the carbon-based seed layer applied to the core material contains from more than about 50% atomic percent carbon.
27. The method of claim 18 further comprising transferring the carbon-coated core part to a reactor configured to apply the functional surface layer on the carbon-coated core part.
28. The method of claim 18 wherein the carbon-based seed layer and functional surface layer are applied in the same reactor.
29. The method of claim 18 wherein the functional surface layer is deposited by a method selected from the group of chemical vapor deposition and salt bath electro deposition.
30. The method of claim 18 wherein the portion of the core part to which the carbon-based seed layer is applied is made from a material that includes nickel (Ni), and depositing the functional surface layer on the carbon-coated core part includes forming a tantalum-containing composition on the carbon-coated core part.

31. A coated part comprising:

a core part made from a nickel-containing composition having an unmodified portion and optionally a modified layer;

a functional surface layer made from a tantalum-containing composition having an unmodified portion and a modified layer in contact with a portion of the core part, the modified layer of the functional surface layer including a nickel diffusion barrier layer formed by a carbon-based seed layer;

an interface layer defined by the modified layer of the functional surface layer, and, where present, the modified layer of the core part, the interface layer having a thickness of less than about 5 μm ; and

wherein the modified layer of the core part, when present, is substantially void of a Kirkendall porosity sublayer.

32. The coated part of claim 31 where the surface coating improves at least one function of the core part selected from corrosion protection, biocompatibility, electrical conductivity, and thermal conductivity.

33. The coated part of claim 31 wherein the interface layer has a thickness in the range of about 0.5 μm to about 5 μm .

34. The coated part of claim 31 wherein Ni constitutes greater than about 15% of the nickel-containing composition by weight.

35. The coated part of claim 31 wherein the core part is made at least in part from a Ni-alloy containing at least about 40% Ni by weight.

36. The coated part of claim 31 wherein the metallic core material includes a Ni-alloy containing chromium, molybdenum, and greater than about 40% Ni by weight.

37. The coated part of claim 31 wherein the tantalum constitutes greater than about 80% of the unmodified portion of the functional surface layer by weight.

38. The coated part of claim 31 wherein the surface layer has a thickness of greater than about 10 μm .
39. The coated part of claim 31 wherein the surface layer is substantially pinhole free.
40. The coated part of claim 31 wherein the interface layer is at least about 1.3 times thinner compared to the interface layer of an object made of the same composition core part and functional surface layer, but without a nickel diffusion barrier layer formed by a carbon-based seed layer.
41. The coated part of claim 31 wherein at least a portion of a wire is secured to the core part.
42. The coated part of claim 41 wherein the wire is of a substantially similar composition as the functional surface layer.
43. A method for making functionally coated objects, the method comprising:
- applying a carbon-based seed layer to coat at least a nickel-containing portion of a core part; and
- depositing a tantalum-containing functional surface layer on at least a portion of the carbon-coated portion of the core part.
44. The method of claim 43 further comprising cleaning the core part before applying the carbon-based seed layer.
45. The method of claim 43 further comprising mounting the core part in a reactor before applying the carbon-based seed layer.
46. The method of claim 45 wherein the core part includes a wire and mounting the core part in a reactor includes hanging the core part by the wire.
47. The method of claim 46 further comprising spot welding a wire to the core part.
48. The method of claim 47 further comprising removing at least a portion of the wire after deposition of the functional surface layer.

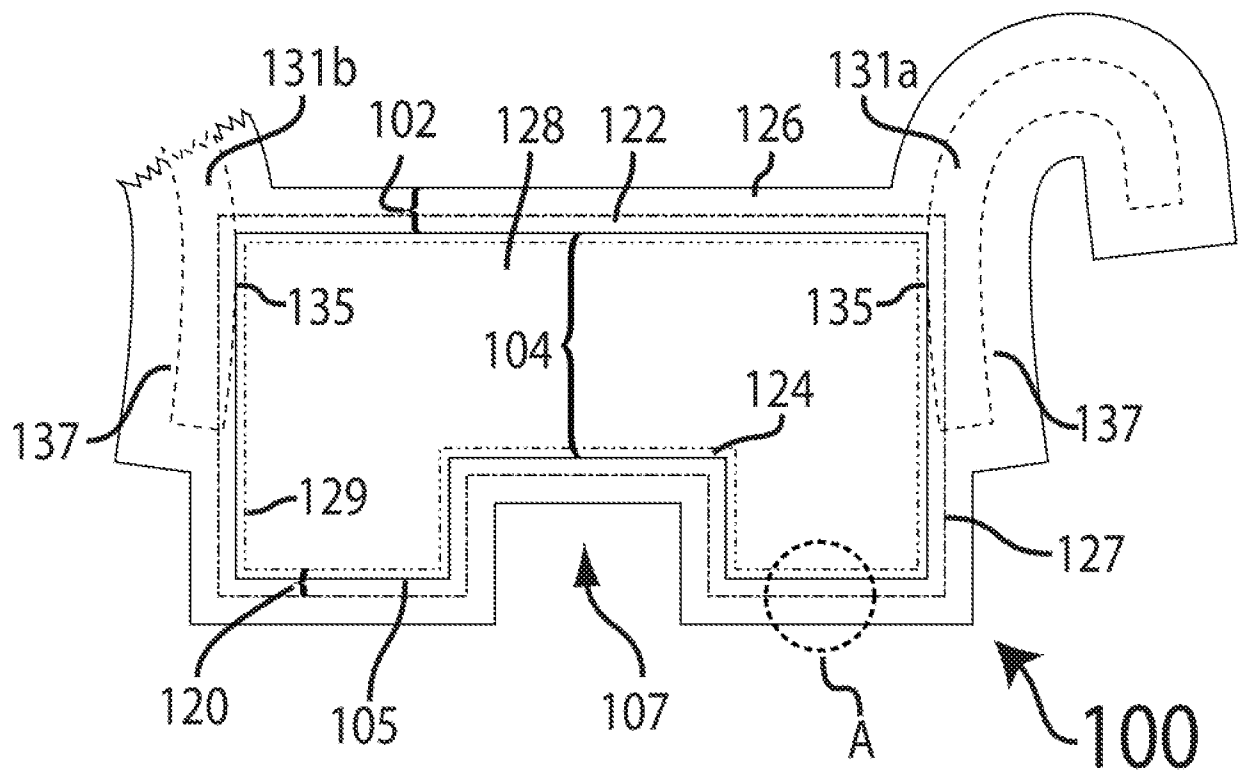


FIG. 1

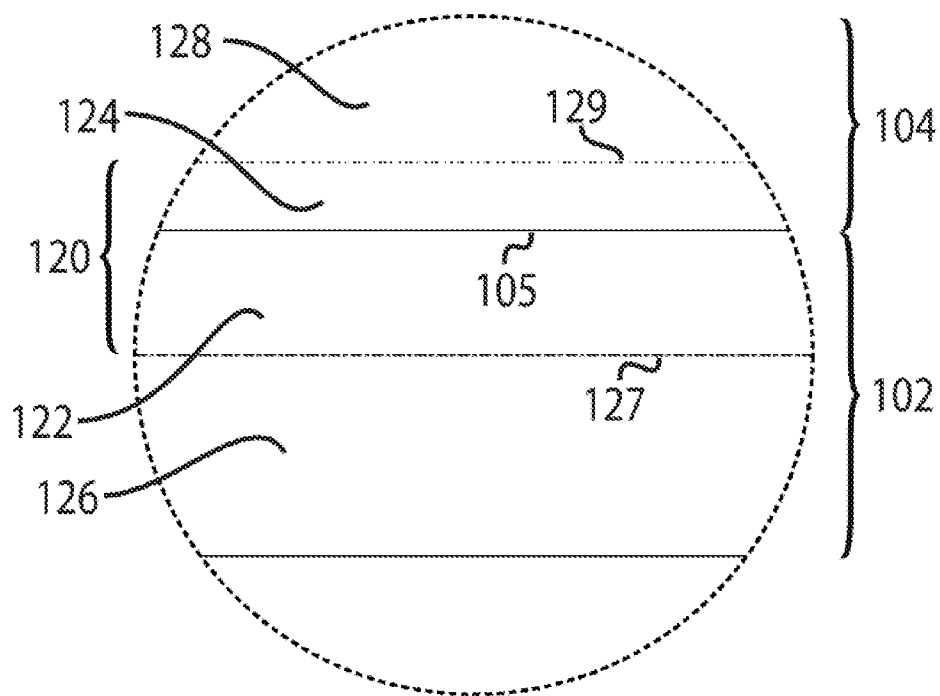


FIG. 1A

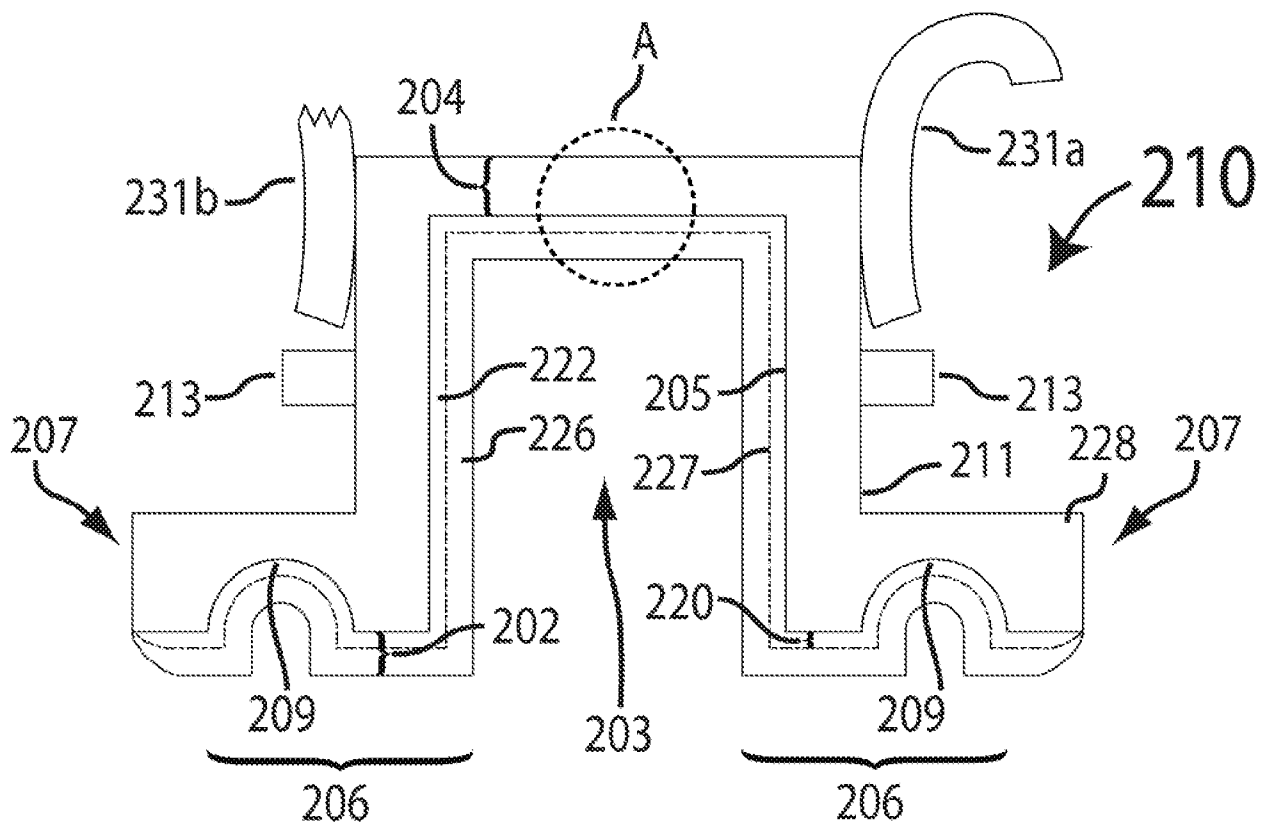


FIG. 2

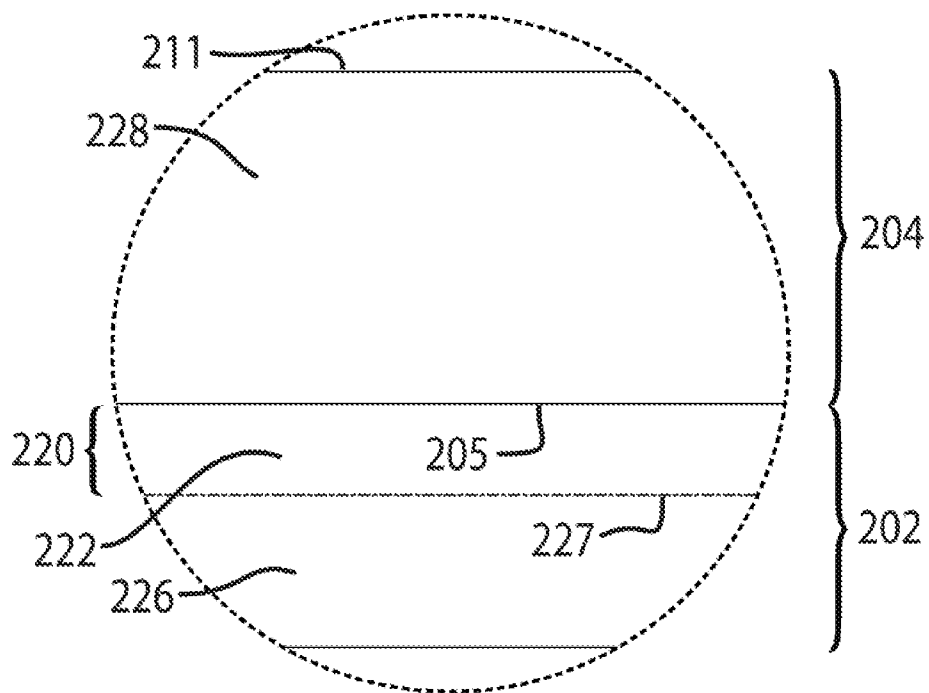


FIG. 2A

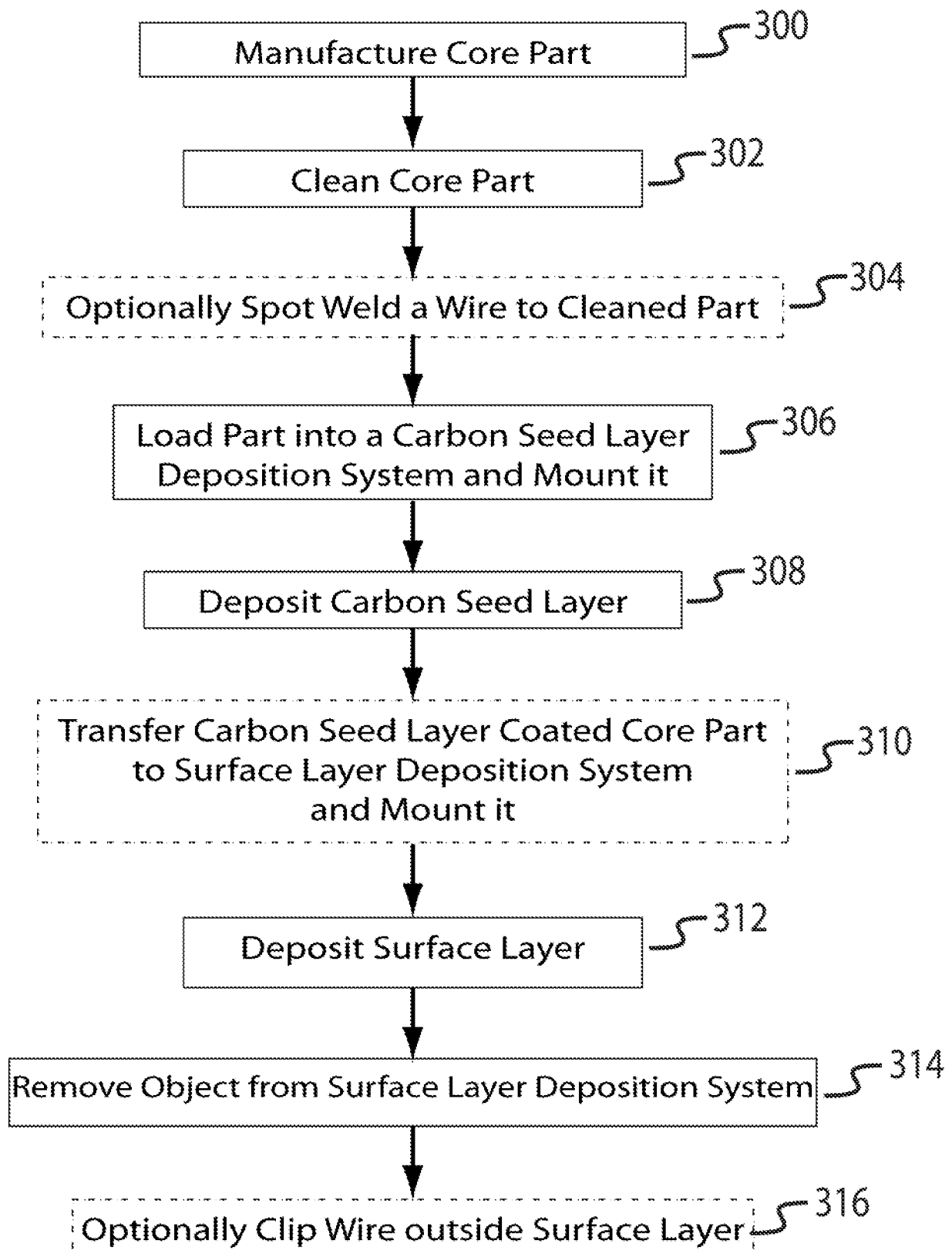


FIG. 3

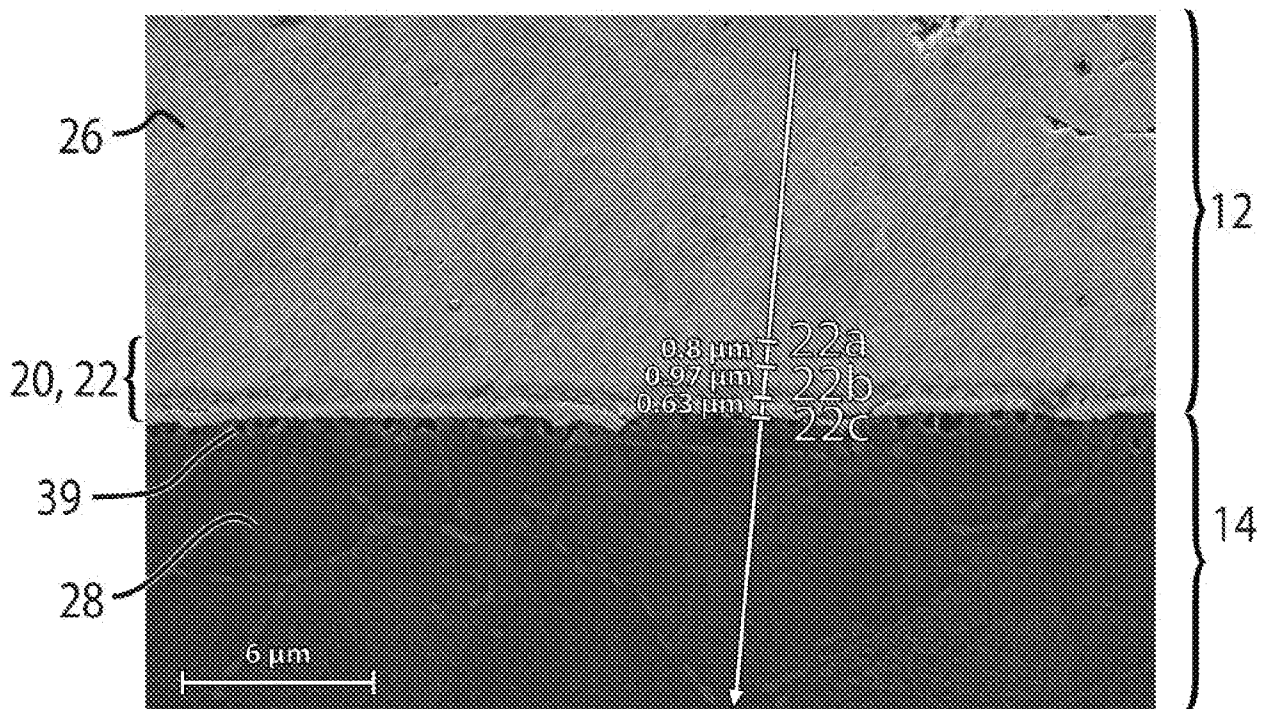


FIG. 4

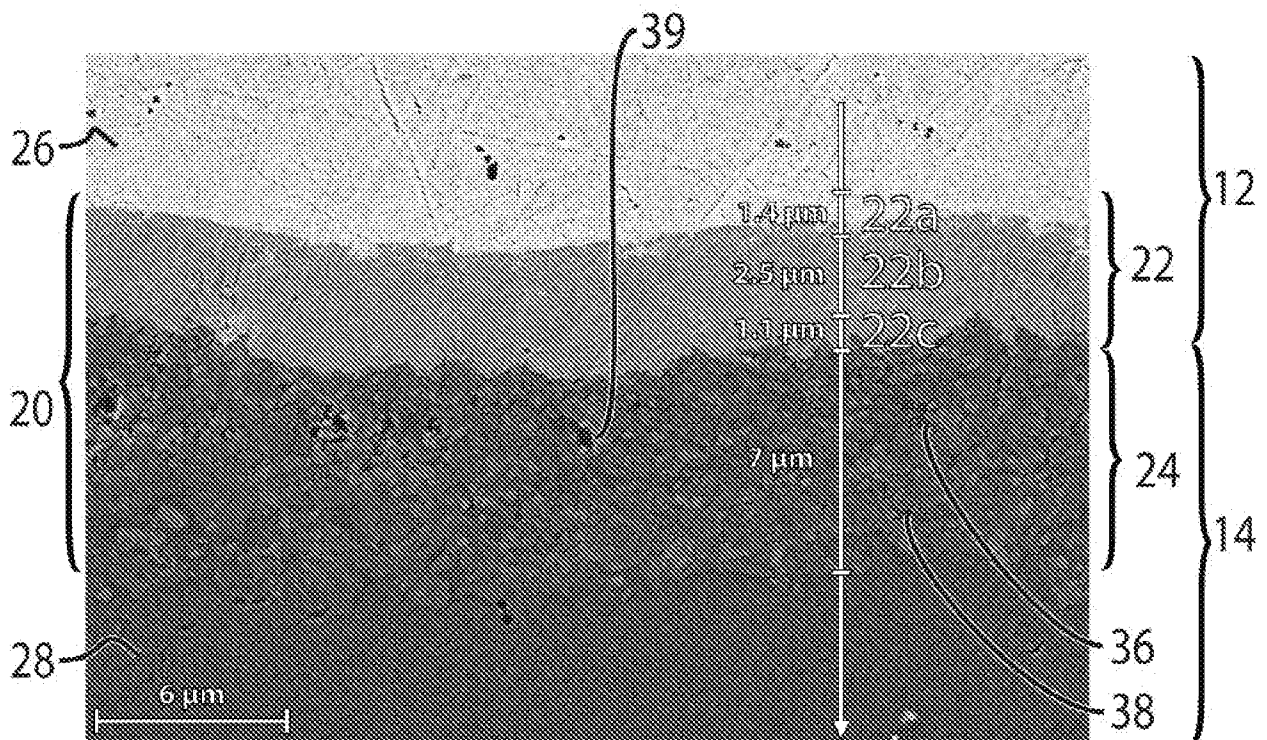


FIG. 6

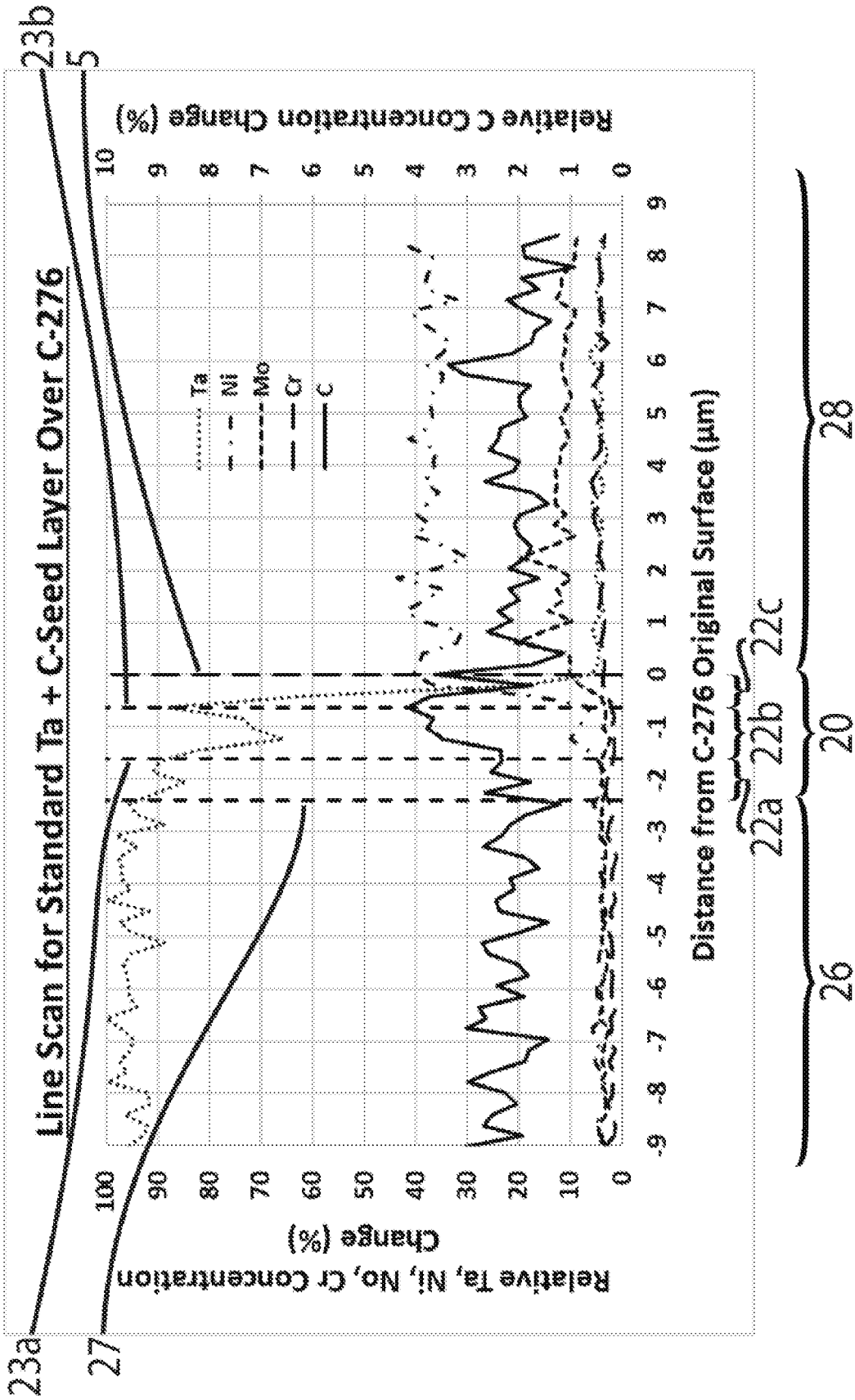


FIG. 5

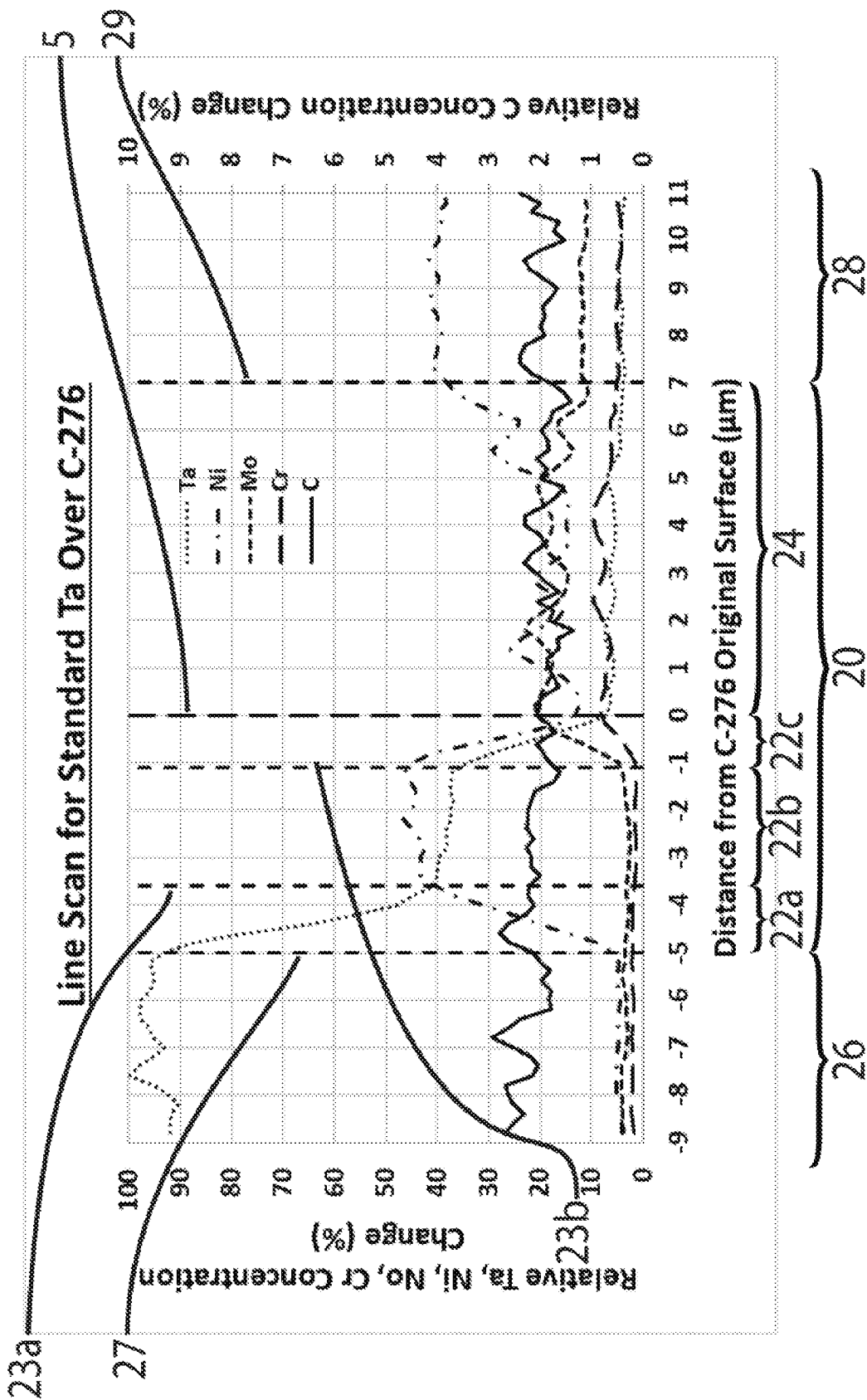


FIG. 7