Abstract: An article may include a substrate that comprises a nickel alloy. The substrate may include a modified subsurface region and a bulk region. The modified subsurface region may include a first composition and the bulk region may include a second composition different than the first composition. The modified subsurface region may include at least one of a reactive element or a noble metal, and the modified subsurface region comprises a thickness of less than about 0.3 μm measured in a direction substantially normal to a surface of the substrate. The modified subsurface region may be formed by depositing a layer including at least one of the reactive element or the noble metal in a layer on a surface of the substrate and introducing the at least one of the reactive element or the noble metal into the modified subsurface region using ion bombardment.
ALLOY WITH ION BOMBARDED SURFACE FOR ENVIRONMENTAL PROTECTION

TECHNICAL FIELD

[0001] The disclosure relates to alloys and coatings for alloys for use in high temperature mechanical systems.

BACKGROUND

[0002] Components of high-temperature mechanical systems, such as, for example, gas-turbine engines, must operate in severe environments. For example, the high-pressure turbine blades, vanes, blade tracks, and blade shrouds are exposed directly to hot flow path gases in commercial aeronautical engines and typically experience metal surface temperatures of about 800°C, with short-term peaks as high as 1100°C. A rim portion of a turbine disk may experience high temperatures of between about 600°C and 750°C. In some cases, the hot flow path gases may include oxidative and/or corrosive chemical species, such as oxygen, sulfur, or the like, to which the rim portion of the turbine disk may be exposed. The high temperatures to which the rim portion is exposed may facilitate oxidation or corrosion upon exposure of the rim portion to oxidative and/or corrosive chemical species, which may affect chemical and mechanical properties of the rim portion.

SUMMARY

[0003] In general, the disclosure is directed to techniques for forming a modified surface and/or subsurface region in an alloy component and to alloy components that include a modified surface and/or subsurface region. In some examples, the alloy may be a nickel disk alloy, such as a γ-Ni + γ'-Ni₃Al alloy. In some examples, the alloy may be formed into a component of a gas turbine engine, such as a turbine disk. The modified surface and/or subsurface region may be formed by depositing a layer that includes at least one element, applying ion bombardment to introduce the element in the layer into the surface and/or subsurface region of the alloy.
[0004] In one aspect, the disclosure is directed to a method that includes depositing a plurality of atoms in a layer on a surface of a substrate that includes a nickel alloy. According to this aspect of the disclosure, the plurality of atoms includes at least one of a reactive element, such as yttrium (Y), hafnium (Hf), zirconium (Zr), lanthanum (La), cerium (Ce), silicon (Si), or chromium (Cr); or a noble metal, such as platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir), osmium (Os), gold (Au), or silver (Ag). The method may further include bombarding the layer with inert ions to implant at least some of the plurality of atoms in a subsurface region of the substrate within about 0.3 micrometers of the surface.

[0005] In another aspect, the disclosure is directed to an article that includes a substrate comprising a nickel alloy. According to this aspect of the disclosure, the substrate may include a modified subsurface region and a bulk region. The modified subsurface region may include a first composition and the bulk region may include a second composition different than the first composition. In some examples, the modified subsurface region includes at least one of a reactive element or a noble metal. Additionally, the modified subsurface region may include a thickness of less than about 0.3 micrometers measured in a direction substantially normal to a surface of the substrate.

[0006] The details of one or more examples are set forth in the accompanying drawings and the description below. Other features, objects, and advantages of the disclosure will be apparent from the description and drawings, and from the claims.

**BRIEF DESCRIPTION OF DRAWINGS**

[0007] FIG. 1 is a conceptual cross-sectional diagram that illustrates an example alloy component.

[0008] FIG. 2 is a flow diagram that illustrates an example technique for forming using ion bombardment a modified subsurface region in an alloy substrate.

[0009] FIG. 3A is a conceptual cross-sectional diagram that illustrates an example alloy substrate and a layer of a plurality of atoms deposited on a surface of the alloy substrate.
FIG. 3 B is a conceptual cross-sectional diagram that illustrates an example alloy substrate that includes a modified subsurface region.

FIG. 4 is a flow diagram that illustrates an example technique for forming using ion bombardment a modified subsurface region in an alloy substrate.

FIG. 5A is a conceptual cross-sectional diagram that illustrates an example alloy substrate and two layers that each include a plurality of atoms deposited on a surface of the alloy substrate.

FIG. 5B is a conceptual cross-sectional diagram that illustrates an example alloy substrate that includes a modified subsurface region.

FIG. 6 is a flow diagram that illustrates an example technique for forming using ion bombardment a modified subsurface region in an alloy substrate.

FIG. 7A is a conceptual cross-sectional diagram that illustrates an example alloy substrate and a layer that includes a plurality of atoms deposited on a surface of the alloy substrate.

FIG. 7B is a conceptual cross-sectional diagram that illustrates an example alloy substrate that includes a modified subsurface region.

FIG. 7C is a conceptual cross-sectional diagram that illustrates an example alloy substrate and a layer that includes a plurality of atoms deposited on a surface of the alloy substrate over a modified subsurface region.

FIG. 7D is a conceptual cross-sectional diagram that illustrates an example alloy substrate that includes a modified subsurface region.

FIG. 8 is a flow diagram that illustrates an example technique of heat-treating an alloy substrate to remove substantially all tertiary γ'-Ni₃Al precipitate from the alloy substrate.

FIG. 9 is a time-temperature diagram that illustrates an example heat treatment to which an alloy substrate may be exposed.

DETAILED DESCRIPTION

In general, the disclosure is directed to techniques for forming a modified surface and/or subsurface region in an article that includes a nickel alloy and articles that include the modified surface and/or subsurface region. In some examples, the article may include a turbine disk. The modified surface and/or
subsurface region may be formed by first depositing a layer of at least one element on a surface of a substrate. In some examples, the layer may be formed on a portion of the substrate, leaving another portion of the substrate uncovered by the layer. In other examples, the layer may be formed on substantially all surfaces of the substrate. The layer may include a plurality of atoms, and the plurality of atoms may include a single element or a mixture of at least two elements. The element or elements may be selected to provide oxidation and/or corrosion protection to the article. For example, the elements may be selected from a reactive element or a noble metal.

[0022] The element or elements may be deposited to a thickness (measured in a direction substantially normal to the surface of the substrate) or a coverage density (measured, e.g., in grams of material per square centimeter of surface area (g/cm²)) that results in a predetermined composition in the modified subsurface region after introduction of the element into the modified subsurface region.

[0023] Once the layer has been deposited on the surface of the substrate, the layer may be bombarded with inert (non-reactive) ions, such as xenon (Xe), helium (He), neon (Ne), argon (Ar), krypton (Kr), or radon (Rn). The ion bombardment may result in atoms in the layer being introduced into the subsurface region. In some examples, the ion bombardment and the introduction of the element into the modified subsurface region may not substantially affect the phase constitution and/or microstructure of the subsurface region. For example, the subsurface region may include a γ-Ni + γ'-Ni3A1 phase constitution prior to introduction of the element into the subsurface region and may also include a γ-Ni + γ'-Ni3A1 phase constitution after introduction of the element into the subsurface region to form the modified subsurface region. In some examples, introduction of the element into the subsurface region may also produce residual stress in the subsurface region.

[0024] FIG. 1 is a conceptual diagram illustrating a cross-section of an example alloy component. In the illustrated example, the alloy component includes a gas turbine engine disk 10 used in a gas turbine engine. Gas turbine engine disk 10 includes a rim portion 12, a web portion 14, and a bore portion 16. In various examples, gas turbine engine disk 10 may be a low, intermediate or high pressure
compressor disk (LPC disk, IPC disk, or HPC disk), a low, intermediate, or high pressure turbine disk (LPT disk, IPT disk, or HPT disk), or a fan disk.

[0025] Although the following description will be directed primarily to a gas turbine engine disk 10 formed of a γ-Ni + γ'-NiAl alloy, in other examples, the alloy component may comprise a different article or component than a gas turbine engine disk 10, or may comprise a different alloy. For example, the alloy component may be another component of a high temperature mechanical system, such as a turbine blade or a shaft for an aero-engine, or may comprise another alloy article that may benefit from a modified subsurface region. In addition, the techniques described herein may be applied to other alloys, such as, for example, steel, aluminum alloys, cobalt alloys, titanium alloys, or the like. In some examples the component may include two or more alloys joined together, e.g., a dual alloy gas turbine engine disk.

[0026] When used in a gas turbine engine, rim portion 12 of gas turbine engine disk 10 may experience different operating conditions than bore portion 16 of gas turbine engine disk 10. For example, bore portion 16 may be substantially isolated from gases passing through the gas turbine engine, while rim portion 12 may be exposed to the gases. Because of this, rim portion 12 may be exposed to higher temperatures and/or a more corrosive and/or oxidative environment than bore portion 16. Accordingly, bore portion 16 and rim portion 12 may benefit from different mechanical and/or chemical properties, including properties along surface and/or subsurface regions of bore portion 16 and rim portion 12. For example, bore portion 16 may benefit from having high tensile strength and high fatigue strength at lower temperatures, while rim portion 12 may benefit from having improved elevated temperature creep resistance, improved damage tolerance, and improved resistance to dwell-fatigue. Additionally or alternatively, rim portion 12 may benefit from a coating or surface region that provides environmental protection to rim portion 12, e.g., from corrosion and/or oxidation, while bore portion 16 may be substantially isolated from hot gases and may not benefit from the coating or surface region that provides environmental protection.

[0027] Chemical and mechanical properties of rim portion 12 and bore portion 16 may be influenced by a chemical or metallurgical composition, phase constitution,
and/or microstructure of the corresponding portion 12 or 16. Gas turbine engine
disk 10 may be formed of a wide range of alloys, including, for example, a Ni-
based superalloy. In some examples, gas turbine engine disk 10 may be formed of
a Ni-based superalloy having a γ-Ni + γ'-Ni₃A lphase constitution. In such
examples, the γ-Ni may be the continuous phase, e.g., the matrix, and the γ'-Ni₃A l
may be the discontinuous phase, e.g., the precipitate. The γ'-Ni₃A lphase may
segregate into distinct, substantially homogeneous domains within the γ-Ni matrix
phase.

[0028] In some examples, the γ'-Ni₃A lprecipitate phase domains may be classified
as primary precipitate phase domains, secondary precipitate phase domains,
tertiary precipitate phase domains, or combinations thereof. The designation
of primary, secondary or tertiary may refer to the method by which the γ'-Ni₃A l
precipitate phase domains were formed or how the precipitate phase domains
respond to heat treatment. For example, primary γ'-Ni₃A lprecipitate phase
domains may remain substantially undissolved and may even coarsen when an
alloy is exposed to a heat treatment below a transition temperature of the alloy. In
some examples, the volume fraction of primary γ'-Ni₃A lprecipitate phase domains
is controlled by the temperature at which the heat treatment is performed and the
size of the primary γ'-Ni₃A lprecipitate phase domains is controlled by the duration
of the heat treatment. In contrast, secondary γ'-Ni₃A lprecipitate phase domains
substantially dissolve in the matrix phase when the alloy is exposed to a heat
treatment above a low temperature threshold and below a transition temperature of
the alloy. Secondary γ'-Ni₃A lprecipitate phase domains form during cooling of
the alloy from relatively high temperatures. Tertiary γ'-Ni₃A lprecipitate phase
domains may also dissolve in the matrix phase when the alloy is exposed to a
heat treatment above a low temperature threshold and below a transition
temperature of the alloy. Tertiary γ'-Ni₃A lprecipitate phase domains may form
during cooling of the alloy at relatively lower temperatures. In addition, tertiary γ'-
N A lprecipitate phase domains may coarsen during aging, while primary and
secondary γ'-Ni₃A lprecipitate phase domains may be relatively unaffected by
aging.
In some examples, the γ′-Ni₃A precipitate phase domains may also be labeled based on an average diameter of the precipitate phase domains. For example, the tertiary γ′-Ni₃A precipitate phase domains may comprise an average diameter of between about 10 nanometers (nm) and about 50 nm (about 0.01 micrometer (μm) and about 0.05 μm), and the secondary γ′-Ni₃A precipitate phase domains may comprise an average diameter between about 100 nm and about 300 nm (about 0.1 μm and about 0.3 μm). Primary γ′-Ni₃A precipitate phase domains may have an average diameter of between about 1 μm and about 3 μm.

In some examples, the volume fraction of the γ′-Ni₃A precipitate phase domains and the type (e.g., primary, secondary, tertiary) of γ′-Ni₃A precipitate phase domains may affect properties of gas turbine engine disk 10, such as, for example, tensile strength, fatigue strength, creep resistance, damage tolerance, or resistance to dwell-fatigue.

The particular chemical composition of the alloy may also affect properties of the gas turbine engine disk 10, even within a single phase constitution. For example, relative amounts of elements in the alloy may affect the mechanical properties of the alloy, such as tensile strength, fatigue strength, creep resistance, damage tolerance, or resistance to dwell-fatigue. Similarly, relative amounts of elements in the alloy may affect the chemical properties of the alloy, such as oxidation resistance, corrosion resistance, or the like. In some cases, the chemical composition of the alloy may produce competing effects, e.g., may detrimentally affect at least one mechanical or chemical property while beneficially affecting at least one other mechanical or chemical property. As described herein, one technique for balancing the effects of different compositions is to form a modified surface and/or subsurface region that results in predetermined characteristics in the surface and/or subsurface region while maintaining a different composition, and, thus, potentially different predetermined characteristics, in the bulk of the alloy.

In some examples, the techniques described herein may be applied to only some portions of the alloy component, such as gas turbine engine disk 10. For example, as described above, substantially only the rim portion 12 of gas turbine engine disk 10 may be exposed to gases passing through the gas turbine engine. Because of this, rim portion 12 may include the modified surface and/or subsurface...
region, which may contribute oxidation and/or corrosion resistance to rim portion 12, while bore portion 16 may not include the modified surface and/or subsurface region. In other examples, substantially all the surfaces of gas turbine engine disk 10, including bore portion 16, web portion 14, and rim portion 12 may include the modified surface and/or subsurface region.

[0033] FIG. 2 is a flow diagram of an example of a technique for forming a modified surface and/or subsurface region in an alloy substrate, such as gas turbine engine disk 10. FIG. 2 will be described with concurrent reference to FIGS. 3A and 3B for ease of description. However, it will be understood that the alloy substrate 32 of FIGS. 3A and 3B may form a portion of rim portion 12, web portion 14, and/or bore portion 16 of gas turbine engine disk 10.

[0034] The technique illustrated in FIG. 1 includes forming a layer 36 that includes a plurality of atoms a surface 34 of alloy substrate 32 (22). As described above, alloy substrate 32 may include a nickel alloy, such as a nickel-based superalloy. In some examples, alloy substrate 32 may include a nickel alloy that includes a γ-Ni + γ′-Ni₃Al phase constitution. As will be described below with respect to FIGS. 8 and 9, in some examples, alloy substrate 32 may be exposed to a heat treatment or other processing step that removes substantially all tertiary γ′-Ni₃Al from at least the portion of alloy substrate 32 that will include the modified surface and/or subsurface region. In other examples, alloy substrate 32 may include any predetermined phase constitution and microstructure, including, for example, at least one of primary γ′-Ni₃Al, secondary γ′-Ni₃Al, and/or tertiary γ′-Ni₃Al.

[0035] Layer 36 may include at least one element, and in some examples may consist essentially of a single element. In other examples, layer 36 may include at least two elements. The element or elements in layer 36 may be selected from, for example, a reactive element or a noble metal. As used herein noble metals include Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au. As used herein, reactive elements include Y, La, Hf, Zr, Ce, Si, and Cr. In some examples, the reactive elements may be subcategorized as a major alloying element (Cr), a minor alloying element (Si), and trace alloying elements (Y, Hf, Zr, La, and Ce, collectively referred to as rare earth reactive elements).
Layer 36 may be deposited to a thickness (measured in a direction substantially normal to surface 34) or coverage density (measured in g/cm²) sufficient to result in a predetermined concentration of the element or elements in the modified surface and/or subsurface region after introduction of atoms in layer 36 into the modified surface and/or subsurface region. For example, the thickness or coverage density that will result in the predetermined concentration of the element may be determined based on a depth of the modified surface and/or subsurface region, measured in a direction substantially normal to surface 34, and the predetermined concentration of the element within the volume of the modified surface and/or subsurface region.

Layer 36 may be deposited using any technique that can deposit layer 36 to a controlled thickness or coverage density. In some examples, a deposition technique that can deposit layer 36 at relatively low temperatures, e.g., below about 1500°F (about 815°C) or, preferably, below about 1400°F (about 760°C), may be utilized. Deposition at a relatively low temperature may facilitate deposition of layer 36 without substantially affecting a microstructure or phase constitution of substrate 32. Additionally or alternatively, deposition at a relatively low temperature may reduce or substantially eliminate interdiffusion of elements between layer 36 and alloy substrate 32. In some examples, layer 36 may be deposited by direct vapor deposition (DVD), electroplating, nanoscale electroplating, metallo-organic chemical vapor deposition (MO-CVD), plasma-assisted physical vapor deposition (PA-PVD), or the like.

Once layer 36 has been deposited on surface 34, layer 36 is bombarded with inert ions using ion bombardment (24). In some examples, the inert ions include a noble gas, such as He, Ne, Ar, Kr, Xe, or Rn. In some implementations heavier ions may be preferred, such as, for example, Xe or Rn.

The inert ions may be accelerated to layer 36 at an energy level sufficient to impact atoms in layer 36 and cause the atoms to be introduced into alloy substrate 32 to a predetermined depth. For example, the inert ions may be accelerated to an energy level sufficient to introduce atoms in layer 36 into alloy substrate 32 to a depth of up to about 0.3 µm (measured in a direction substantially normal to surface 34). In other examples, the inert ions may be accelerated to an energy level
sufficient to introduce atoms in layer 36 into alloy substrate 32 to a lesser depth, e.g., any depth between zero (0) μm and about 0.3 μm.

[0040] In some examples, the inert ions may be accelerated to different energy levels, such that the atoms in layer 36 are introduced to different depths in alloy substrate 32. For example, the inert ions may be accelerated to energy levels that result in the atoms in layer 36 being introduced into alloy substrate 32 at depths ranging substantially continuously from 0 μm to the maximum depth of modified subsurface region 38. In different examples, the maximum depth of modified subsurface region 38 may range from about 0.01 μm to about 0.3 μm. In this way, the ion bombardment may be used to introduce atoms in layer 36 substantially throughout the depth of modified subsurface region 38.

[0041] In some implementations, introduction of the atoms from layer 36 into modified subsurface region 38 may produce stress in alloy substrate 32, at least in modified subsurface region 38. The stress may toughen the surface region similar to other methods of producing compressive surface stresses, such as peening. The toughened modified subsurface region 38 may result in enhanced resistance to high temperature creep or enhanced resistance to crack propagation in modified subsurface region 38 compared to an alloy substrate 32 that has not been exposed to such stresses.

[0042] In some cases, utilizing ion bombardment to form modified subsurface region 38 in alloy substrate 32 may facilitate formation of modified subsurface region 38 without substantially changing the microstructure and/or phase constitution of alloy substrate 32 in modified subsurface region 38. For example, as described above, alloy substrate 32 may include a γ-Ni + γ'-Ni₃A 1phase constitution prior to introduction of atoms in layer 36 into modified subsurface region 38 by ion bombardment. In some examples, the introduction of the atoms from layer 36 into modified subsurface region 38 by ion bombardment leaves the γ-Ni + γ'-Ni₃A 1phase constitution in modified subsurface region 38 substantially unchanged.

[0043] In some implementations, utilizing ion bombardment to form modified subsurface region 38 may facilitate formation of modified subsurface region 38 while leaving the external dimensions of alloy substrate 32 substantially
unchanged. This may be beneficial in applications where the dimensions of alloy substrate 32 have small tolerances and are formed precisely.

[0044] The ion bombardment step (24) may be carried out at a relatively low temperature, e.g., below about 1500°F (about 815°C) or, preferably, below about 1400°F (about 760°C), which as described above, may not substantially affect a microstructure or phase constitution of alloy substrate 32. Additionally, maintaining layer 36 and alloy substrate 32 at a relatively low temperature may reduce or substantially eliminate interdiffusion of elements in alloy substrate 32 and layer 36.

[0045] After completion of the ion bombardment and introduction of the element or elements in layer 36 into modified subsurface region 38, modified subsurface region 38 may include a predetermined amount of the element or elements that were deposited in layer 36. For example, layer 36 may include at least one noble metal and/or at least one reactive element. In some examples, in which modified subsurface region 38 includes at least one reactive element, the at least one reactive element may be at least of a one major alloying element (Cr), a minor alloying element (Si), or a trace alloying element (Y, Hf, Zr, La, and Ce, collectively, rare earth reactive elements).

[0046] When layer 36 includes at least one noble metal, modified subsurface region 38 may include less than about 20 weight percent (wt. %) of the at least one noble metal, whether layer 36 includes a single noble metal or two or more noble metals. In some examples, modified subsurface region 38 may include less than about 10 wt. % of the at least one noble metal, whether layer 36 includes a single noble metal or two or more noble metals. In examples in which layer 36 includes at least one noble metal, modified subsurface region 38 may include at least about 1 wt. % of the at least one noble metal (e.g., between about 1 wt. % and about 20 wt. % or between about 1 wt. % and about 10 wt. %). In some examples, modified subsurface region 38 may include at least about 2.5 wt. % of the at least one noble metal (e.g., between about 2.5 wt. % and about 20 wt. % or between about 2.5 wt. % and about 10 wt. %).

[0047] When layer 36 includes Cr, modified subsurface region 38 may include less than about 30 wt. % Cr. In some examples, modified subsurface region 38 may
include less than about 20 wt. % Cr. In other examples, modified subsurface region 38 may include less than about 10 wt. % Cr. In examples in which layer 36 includes Cr, modified subsurface region 38 may include at least about 1 wt. % Cr (e.g., between about 1 wt. % and about 30 wt. % or between about 1 wt. % and about 20 wt. % or between about 1 wt. % and about 10 wt. %). In some examples, modified subsurface region 38 may include at least about 5 wt. % Cr (e.g., between about 5 wt. % and about 30 wt. % or between about 5 wt. % and about 20 wt. % or between about 5 wt. % and about 10 wt. %).

[0048] When layer 36 includes at least one rare earth reactive element (e.g., Y, Hf, Zr, La, and/or Ce), modified subsurface region 38 may include less than about 1 wt. % of the at least one rare earth reactive element, whether layer 36 includes a single rare earth reactive element or at least two rare earth reactive elements. In some examples, modified subsurface region 38 may include less than about 0.1 wt. % of the at least one rare earth reactive element, whether layer 36 includes a single rare earth reactive element or at least two rare earth reactive elements. In examples in which layer 36 includes at least one rare earth reactive element, modified subsurface region 38 may include at least about 0.005 wt. % of the at least one rare earth reactive element (e.g., between 0.005 wt. % and about 1 wt. % or between 0.005 wt. % and about 0.1 wt. %). In some examples, modified subsurface region 38 may include at least about 0.01 wt. % of the at least one rare earth reactive element (e.g., between about 0.01 wt. % and about 1 wt. % or between about 0.01 wt. % and about 0.1 wt. %).

[0049] When layer 36 includes Si, modified subsurface region 38 may include less than about 2 wt. % Si. In some examples, modified subsurface region 38 may include less than about 1 wt. % Si. In examples in which layer 36 includes Si, modified subsurface region 38 may include at least about 0.005 wt. % Si (e.g., between 0.005 wt. % and about 2 wt. % or between 0.005 wt. % and about 1 wt. %). In some examples, modified subsurface region 38 may include at least about 0.01 wt. % Si (e.g., between 0.01 wt. % and about 2 wt. % or between 0.01 wt. % and about 1 wt. %).

[0050] In some examples, layer 36 may have included at least one rare earth reactive element and Si. Modified subsurface region 38 then may include less than
about 2 wt. % total of the at least one rare earth reactive element and Si. In some examples, modified subsurface region 38 may include less than about 1 wt. % total of the at least one rare earth reactive element and Si.

[0051] In some examples, the composition of modified subsurface region 38 may change as a function of depth within alloy substrate 32. For example, the composition of modified subsurface region 38 may be more similar to the composition of alloy substrate 32 at the boundary of modified subsurface region 38 and alloy substrate 32 and may be more different from the composition of alloy substrate 32 nearer to surface 34. In some examples, such a gradient composition may reduce risk of delamination or spalling of modified subsurface region 38 from alloy substrate 32, e.g., may increase adhesion between modified subsurface region 38 and alloy substrate 32. In some examples, the compositions listed above may refer to an average composition within modified subsurface region 38.

[0052] Although not shown in FIG. 2, in some implementations, the technique may include a post-ion bombardment heat treatment step. The heat treatment step may be performed to oxidize Cr or Al present in modified subsurface region 38 to form an oxide scale on surface 34. The oxide scale may reduce or substantially eliminate further oxidation and/or corrosion of alloy substrate 32, and in this way may provide environmental protection to alloy substrate 32. The elements present in modified subsurface region 38 may contribute to formation of the oxide scale, may improve adhesion of the oxide scale to surface 34, or may reduce a rate of further oxidation. For example, Cr may oxidize to form the oxide scale. A reactive element may provide oxidation resistance, e.g., reduce a rate of further oxidation, and may additionally or alternatively increase adhesion of the oxide scale to surface 34. Noble metals may also contribute resistance to further oxidation.

[0053] While FIGS. 2, 3A, and 3B have describe a technique that includes depositing a single layer 36 on surface 34, in other implementations, a technique may include depositing multiple layers on surface 34. In some examples, the multiple layers may include different elements. FIGS. 4, 5A, and 5B illustrate one example of such a technique.

[0054] As shown in FIG. 4, the technique may include depositing a first layer 52 on surface 34 of alloy substrate 32 (42). First layer 52 may include a plurality of
atoms and includes at least one element. In some examples, first layer 52 may consist essentially of a single element, while in other examples, first layer 52 may include at least two elements. As described above, the element or elements may be selected from a reactive element and/or a noble metal.

[0055] First layer 52 may be deposited to a thickness (measured in a direction substantially normal to surface 34) or coverage density (measured in g/cm²) sufficient to result in a predetermined concentration of the element or elements in the modified surface and/or subsurface region after introduction of atoms in first layer 52 into the modified surface and/or subsurface region. For example, the thickness or coverage density necessary to result in the predetermined concentration of the element may be determined based on a depth of the modified surface and/or subsurface region, measured in a direction substantially normal to surface 34, and the predetermined concentration of the element within the volume of the modified surface and/or subsurface region.

[0056] First layer 52 may be deposited using any technique that can deposit first layer 52 to a controlled thickness or coverage density. In some examples, a deposition technique that can deposit first layer 52 at relatively low temperatures, e.g., below about 1500 °F (about 815°C) or, preferably, below about 1400°F (about 760°C), may be utilized. Deposition at a relatively low temperature may facilitate deposition of first layer 52 without substantially affecting a microstructure or phase constitution of alloy substrate 32. Additionally or alternatively, deposition at a relatively low temperature may reduce or substantially eliminate interdiffusion of elements between first layer 52 and alloy substrate 32. In some examples, first layer 52 may be deposited by DVD, electroplating, nanoscale electroplating, MO-CVD, PA-PVD, or the like.

[0057] After deposition of first layer 52 is complete, second layer 54 may be deposited on first layer 52 (44). In some examples, second layer 54 may include at least one element that is not present in first layer 52. Similar to first layer 52, second layer 54 may include at least one element, and in some examples, may consist essentially of a single element. In other examples, second layer 54 may include at least two elements. The element or elements in second layer 54 may be selected from among a reactive element or a noble metal.
[0058] Second layer 54 may be deposited to a thickness (measured in a direction substantially normal to surface 34) or coverage density (measured in g/cm²) sufficient to result in a predetermined concentration of the element or elements in the modified surface and/or subsurface region after introduction of atoms in second layer 54 into the modified surface and/or subsurface region. For example, the thickness or coverage density necessary to result in the predetermined concentration of the element may be determined based on a depth of the modified surface and/or subsurface region, measured in a direction substantially normal to surface 34, and the predetermined concentration of the element within the volume of the modified surface and/or subsurface region.

[0059] Second layer 54 may be deposited using any technique that can deposit second layer 54 to a controlled thickness or coverage density. In some examples, a deposition technique that can deposit second layer 54 at relatively low temperatures, e.g., below about 1500 °F (about 815°C) or, preferably, below about 1400°F (about 760°C), may be utilized. Deposition at a relatively low temperature may facilitate deposition of second layer 54 without substantially affecting a microstructure or phase constitution of alloy substrate 32. Additionally or alternatively, deposition at a relatively low temperature may reduce or substantially eliminate interdiffusion of elements between second layer 54 and alloy substrate 32. In some examples, second layer 54 may be deposited by DVD, electroplating, nanoscale electroplating, MO-CVD, PA-PVD, or the like. In some examples, first layer 52 and second layer 54 are deposited using a similar technique, while in other examples, first layer 52 may be deposited using a first technique and second layer 54 may be deposited using a second technique.

[0060] In some examples, a technique that includes depositing a first layer 52 and a second layer 54 may facilitate independent control of the amount of a first element and a second element deposited on surface 34 and introduced into modified subsurface region 56. For example, first layer 52 may include the first element and second layer 54 may include the second element. In some cases, depositing the first element in first layer 52 and the second element in second layer 54 may facilitate more precise control of the amounts of the first and second
elements deposited compared to depositing the first and second elements as a mixture in a single layer.

[0061] Once first layer 52 and second layer 54 have been deposited on surface 34, first and second layers 52 and 54 are bombarded with inert ions using ion bombardment (46). In some examples, the inert ions include a noble gas, such as He, Ne, Ar, Kr, Xe, or Rn. In some implementations heavier ions may be preferred, such as, for example, Xe or Rn.

[0062] The inert ions may be accelerated to first and second layers 52 and 54 at an energy level sufficient to impact atoms in first and second layers 52 and 54 and cause the atoms to be introduced into alloy substrate 32 to a predetermined depth. For example, the inert ions may be accelerated to an energy level sufficient to introduce atoms in first and second layers 52 and 54 into alloy substrate 32 to a depth of up to about 0.3 μm (measured in a direction substantially normal to surface 34). In other examples, the inert ions may be accelerated to an energy level sufficient to introduce atoms in first and second layers 52 and 54 into alloy substrate 32 to a lesser depth, e.g., any depth between zero (0) μm and about 0.3 μm.

[0063] In some examples, the inert ions may be accelerated to different energy levels, such that the atoms in first and second layers 52 and 54 are introduced to different depths in alloy substrate 32. For example, the inert ions may be accelerated to energy levels that result in the atoms in first and second layers 52 and 54 being introduced into alloy substrate 32 at depths ranging substantially continuously from 0 μm to the maximum depth of modified subsurface region 56. In different examples, the maximum depth of modified subsurface region 56 may range from about 0.01 μm to about 0.3 μm. In this way, the ion bombardment may be used to introduce atoms in first and second layers 52 and 54 substantially throughout the depth of modified subsurface region 56.

[0064] Modified subsurface region 56 may include a composition similar to or substantially the same as any of those described above. For example, modified subsurface region 56 may include less than about 1 wt. % of at least one rare earth reactive element, less than about 2 wt. % Si, less than about 30 wt. % Cr, and/or less than about 20 wt. % of at least one noble metal. Modified subsurface region
56 also may include other elements, such as those present in alloy substrate 32 prior to deposition of first layer 52 and second layer 54. As described above, the listed compositions may be average compositions calculated for the entire modified subsurface region 56, although the composition of modified subsurface region 56 may change within modified subsurface region 56, e.g., may change as a function of depth within modified subsurface region 56.

[0065] The ion bombardment step (46) may be carried out at a relatively low temperature, e.g., below about 1500 °F (about 815°C) or, preferably, below about 1400°F (about 760°C), which, as described above, may not substantially affect a microstructure or phase constitution of alloy substrate 32. Additionally, maintaining first layer 52, second layer 54, and alloy substrate 32 at a relatively low temperature may reduce or substantially eliminate interdiffusion of elements in alloy substrate 32 and layer 36. Optionally, after the ion bombardment step (46), alloy substrate 32, including modified subsurface region 56, may be exposed to a heat treatment step. The heat treatment step may be performed to oxidize Cr or Al present in modified subsurface to form an oxide scale on surface 34. The oxide scale reduces or substantially eliminates further oxidation and/or corrosion of alloy substrate 32, and in this way may provide environmental protection to alloy substrate 32.

[0066] In some examples, as shown in FIGS. 6, 7A, 7B, 7C, and 7D, instead of depositing both first layer 52 and second layer 54 on surface 34 prior to performing ion bombardment, a first layer 72 may be deposited on surface 34 (62) and introduced into a subsurface region of alloy substrate 32 using ion bombardment (64) to form a modified subsurface region 74. A second layer 76 then may be deposited on surface 34 (66) and an element or elements from second layer 76 may be introduced into modified subsurface region 74 using ion bombardment (68) to form a further modified subsurface region 78, which includes elements from first layer 72 and second layer 76.

[0067] First layer 72 may include, for example, at least one element selected from a reactive element and/or a noble metal. Similarly, second layer 76 may include at least one element selected from a reactive element and/or a noble metal. In some examples, first layer 72 and second layer 76 include at least one different element,
and in some examples, first layer 72 may include a single, first element, and second layer 76 may include a single, different, second element.

[0068] As described above, each of first layer 72 and second layer 76 may be deposited to a thickness or a coverage density that results in a predetermined composition in modified subsurface region 78 after the element(s) in first layer 72 and second layer 76 are introduced. For example, first layer 72 and second layer 76 may include sufficient amounts of at least one element so modified subsurface region 78 includes less than about 1 wt. % of at least one rare earth reactive element, less than about 2 wt. % Si, less than about 30 wt. % Cr, and/or less than about 20 wt. % of at least one noble metal, or any other predetermined composition within ranges listed herein.

[0069] In some examples, techniques described herein may include an initial heat treatment step to form a predetermined microstructure in the alloy component (e.g., the alloy substrate). For example, as shown in FIGS. 8 and 9, an alloy component may be heated 92 to a heat treatment temperature 94 that is less than a transition temperature 100 of the alloy (82). In some examples, as described above, the alloy component may be formed of a γ-Ni + γ'Ni₃Al alloy. The transition temperature 100 for the γ-Ni + γ'Ni₃Al alloy is referred to as the γ'Ni₃Al solvus temperature, which is the temperature above which the γ'Ni₃Al phase, including primary γ'Ni₃Al precipitate phase domains, secondary γ'Ni₃Al precipitate phase domains, and tertiary γ'Ni₃Al precipitate phase domains, substantially fully dissolves in the γ-Ni phase to form a solid solution. In some examples, the γ'Ni₃Al solvus temperature may be between about 1915°F (about 1046°C) and about 2150°F (about 1177°C) and the melting temperature 98 may be between about 2150°F (about 1177°C) and about 2350°F (about 1288°C). The γ'Ni₃Al solvus temperature and melting temperature 98 will depend on the precise composition of the alloy, and other γ-Ni + γ'Ni₃Al alloys may have a different transition temperature 100 and/or a different melting temperature 98.

[0070] In some examples, the heat treatment at a temperature below the transition temperature 100 of the alloy may result in dissolution of at least some of the precipitate phase domains. As one example, a γ-Ni + γ'Ni₃Al alloy may include γ'Ni₃Al domains that are classified as at least one of primary, secondary or tertiary
precipitate phase domains. When a $\gamma\cdot\text{Ni} + \gamma'\cdot\text{Ni}_3\text{Al}$ alloy is heat treated at a temperature 94 below a transition temperature 100 of the alloy (82), any secondary or tertiary $\gamma'\cdot\text{Ni}_3\text{Al}$ precipitate phase domains present in the alloy may substantially dissolve in the $\gamma\cdot\text{Ni}$ matrix, while any primary $\gamma'\cdot\text{Ni}_3\text{Al}$ primary precipitate phase domains may remain substantially undissolved and may even coarsen. For example, the $\gamma\cdot\text{Ni} + \gamma'\cdot\text{Ni}_3\text{Al}$ alloy component may be heated to a temperature between about 75°F (about 41.67°C) and about 150°F (about 83.33°C) below the $\gamma'\cdot\text{Ni}_3\text{Al}$ solvus temperature. When the $\gamma\cdot\text{Ni} + \gamma'\cdot\text{Ni}_3\text{Al}$ alloy is cooled from the heat treatment temperature 94 (84), secondary $\gamma'\cdot\text{Ni}_3\text{Al}$ precipitate phase domains may form during the cooling 96 at relatively high temperatures, while tertiary $\gamma'\cdot\text{Ni}_3\text{Al}$ precipitate phase domains may form during the cooling 96 at lower temperatures. In some examples, if the rate of cooling the alloy component is sufficiently slow, tertiary precipitate phase domains may not form.

[0071] Once the predetermined phase constitution and microstructure is formed, e.g., a microstructure substantially free of tertiary $\gamma'\cdot\text{Ni}_3\text{Al}$ precipitate phase domains, the technique may continue with formation of the modified subsurface region. For example, as illustrated in FIG. 8, layer 36 may be deposited on surface 34 (22) and an element or elements from layer 36 may be introduced into modified subsurface region 38 using ion bombardment (24). In other examples, the technique illustrated in FIGS. 8 and 9 may include depositing a first layer and a second layer on surface 34, as illustrated in FIGS. 4 and 5 or FIGS. 6 and 7.

[0072] Various examples have been described. These and other examples are within the scope of the following claims.
CLAIMS:

1. A method comprising:
   depositing a plurality of atoms in a layer on a surface of a substrate that
   comprises a nickel alloy, wherein the plurality of atoms comprises at least one of a
   reactive element or a noble metal; and
   bombarding the layer with inert ions to implant at least some of the
   plurality of atoms in a subsurface region of the substrate within about 0.3 \( \mu \)m of
   the surface.

2. The method of claim 1, wherein the inert ions comprise at least one of Xe, He, Ne, Ar, Kr, or Rn.

3. The method of claim 1 or 2, wherein the plurality of atoms comprises the
   reactive element, and wherein the reactive element comprises at least one of Y, La, Hf, Zr, Ce, Si, or Cr.

4. The method of any of claims 1 to 3, wherein the plurality of atoms
   comprises the noble metal, and wherein the noble metal comprises at least one of
   Ru, Rh, Pd, Pt, Os, Ir, Ag, or Au.

5. The method of any of claims 1 to 4, wherein the plurality of atoms consist
   essentially of a single element selected from the group consisting of the reactive
   element or the noble metal.

6. The method of any of claims 1 to 5, wherein the subsurface region of the
   substrate comprises a \( \gamma \)-Ni + \( \gamma' \)-Ni\(_2\)A 1phase constitution prior to bombarding the
   layer with inert ions, and wherein bombarding the layer with inert ions leaves the
   \( \gamma \)-Ni + \( \gamma' \)-Ni\(_2\)A 1phase constitution in the subsurface region of the substrate
   substantially unchanged.
7. The method of any of claims 1 to 6, wherein the plurality of atoms comprises the reactive element, wherein the reactive element comprises at least one rare earth reactive element, and wherein the subsurface region comprises less than about 1 wt. % of the at least one rare earth reactive element.

8. The method of any of claims 1 to 7, wherein the plurality of atoms comprises the reactive element, wherein the reactive element comprises Si, and wherein the subsurface region comprises less than about 2 wt. % Si.

9. The method of any of claims 1 to 8, wherein the plurality of atoms comprises the reactive element, wherein the reactive element comprises Cr, and wherein the subsurface region comprises less than about 30 wt. % Cr.

10. The method of any of claims 1 to 9, wherein the plurality of atoms comprise the noble metal, and wherein the subsurface region comprises less than about 20 wt. % of the noble metal.

11. The method of any of claims 1 to 10, wherein the superalloy substrate comprises a γ-Ni + γ’-Ni3Al phase constitution, further comprising:

    heat treating the superalloy substrate to dissolve substantially all tertiary γ’-Ni3Al present in the subsurface region, so that the subsurface region is essentially free of tertiary γ’-Ni3Al prior to depositing the plurality of atoms in the layer on the surface of the superalloy substrate.

12. The method of any of claim 1 to 11, further comprising:

    heat treating the substrate including the subsurface region to oxidize Cr or Al present in the subsurface region to form an oxide scale on a surface of the subsurface region.
13. An article comprising a substrate comprising a nickel alloy, wherein the substrate comprises a modified subsurface region and a bulk region, wherein the modified subsurface region comprises a first composition and the bulk region comprises a second composition different than the first composition, wherein the modified subsurface region comprises at least one of a reactive element or a noble metal, and wherein the modified subsurface region comprises a thickness of less than about 0.3 µm measured in a direction substantially normal to a surface of the substrate.

14. The article of claim 13, wherein the modified subsurface region comprises a γ-Ni + γ’-Ni₃A 1phase constitution.

15. The article of claims 13 or 14, wherein the modified subsurface region comprises the reactive element, wherein the reactive element comprises at least one of Y, La, Hf, Zr, or Ce, and wherein the modified subsurface region comprises less than about 1 wt. % of the at least one of Y, La, Hf, Zr, or Ce.

16. The article of any of claims 13 to 15, wherein the modified subsurface region comprises the reactive element, wherein the reactive element comprises Si, and wherein the modified subsurface region comprises less than about 2 wt. % Si.

17. The article of any of claims 13 to 16, wherein the modified subsurface region comprises the reactive element, wherein the reactive element comprises Cr, and wherein the modified subsurface region comprises less than about 30 wt. % Cr.

18. The article of any of claims 13 to 17, wherein the modified subsurface region comprises the noble metal, and wherein the subsurface region comprises less than about 20 wt. % of the noble metal.

19. The article of claim 18, wherein the noble metal comprises at least one of Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au.
20. The article of any of claims 13 to 19, further comprising an oxide scale formed on a surface of the modified subsurface region, wherein the oxide scale comprises at least one of chromium oxide (Cr₂O₃) or aluminum oxide (Al₂O₃).
FIG. 1

FIG. 2

DEPOSIT LAYER ON SURFACE OF SUBSTRATE

BOMBARD LAYER WITH INERT IONS
42 DEPOSIT FIRST LAYER ON SURFACE OF SUBSTRATE

44 DEPOSIT SECOND LAYER ON FIRST LAYER

46 BOMBARD FIRST AND SECOND LAYERS WITH INERT IONS

FIG. 4

FIG. 5A
FIG. 5B

62 DEPOSIT FIRST LAYER ON SURFACE OF SUBSTRATE

64 BOMBARD FIRST LAYER WITH INERT IONS

66 DEPOSIT SECOND LAYER ON SURFACE OF SUBSTRATE

68 BOMBARD SECOND LAYER WITH INERT IONS

FIG. 6
HEAT ALLOY COMPONENT BELOW TRANSITION TEMPERATURE

COOL

DEPOSIT LAYER ON SURFACE OF SUBSTRATE

BOMBARD LAYER WITH INERT IONS

FIG. 8

FIG. 9