Methods and apparatuses for use in such methods for removing islands from laser cut articles. Methods include using a chemical etching solution to remove material in the strut-island gap. Optionally, heat and/or agitation can be applied during the etching process to increase the chemical activity of the chemical etching solution and/or to vibrate the islands out of position.
Disposing A Laser Cut Article In A Chemical Etching Solution

Etching The Laser Cut Article To Remove Islands

Fig. 6

Providing A Laser Cut Refractory Metal Article That Includes Islands

Treating The Article To Remove The Islands

Fig. 7
Providing A Laser Cut Refractory Metal Stent

Disposing The Laser Cut Refractory Metal Stent In A Chemical Etching Solution That Includes HF And HNO₃

Heating The Stent In The Etching Solution To Temp In A Range From About 40°C To about 70°C

Sonicating In The Chemical Etching Solution Using An Ultra-Sonic Cleaning Apparatus

Treating Under Heating And Sonication For at Period Of Time Sufficient To Remove The One Or More Islands

Fig. 8
Providing A First Refractory Metal Workpiece

Laser Cutting The First Refractory Metal Workpiece To Form A Laser-Cut Refractory Metal Stent

Disposing The Laser-Cut Refractory Metal Stent In A Chemical Etching Solution that Includes Hydrofluoric Acid (HF) And Nitric Acid (HNO₃)

Heating The Laser-Cut Refractory Metal Stent In The Chemical Etching Solution To A Temperature In A Range From About 40°C to About 70°C

Sonicating The Laser-Cut Refractory Metal Stent In The Chemical Etching Solution Using An Ultrasonic Cleaning Apparatus

Treating The Laser-Cut Refractory Metal Stent In The Chemical Etching Solution Using An Ultrasonic Cleaning Apparatus

Chemically Treating And /Or Heat-Treating The Refractory Metal Stent

Fig. 9
Providing A First Refractory Metal Workpiece

Laser Cutting The First Refractory Metal Workpiece To Form A Laser-Cut Refractory Metal Stent

Disposing The Laser-Cut Refractory Metal Stent In A Chemical Etching Solution that Includes Hydrofluoric Acid (HF) And Nitric Acid (HNO₃)

Heating The Laser-Cut Refractory Metal Stent In The Chemical Etching Solution To A Temperature In A Range From About 40°C to About 70°C

Sonicating The Laser-Cut Refractory Metal Stent In The Chemical Etching Solution Using An Ultrasonic Cleaning Apparatus

Treating The Laser-Cut Refractory Metal Stent In The Etching Solution Under Sonication And Heating For A Period Of Time Sufficient To The One Or More Islands Therefrom

Rinse, Dry And Inspect

Electropolishing The Laser-Cut Refractory Metal Stent In An Electropolishing Solution

Heat Treating The Laser-Cut Refractory Metal Stent So As To Form An Implantable Stent

Fig. 10
REMOVAL OF AN ISLAND FROM A LASER CUT ARTICLE

BACKGROUND

[0001] 1. Technological Field
[0002] The present disclosure relates to laser cut articles and methods for their manufacture.
[0003] 2. The Relevant Technology
[0004] The human body includes various lumens, such as blood vessels or other passageways. A lumen may sometimes become at least partially blocked or weakened. For example, a lumen may be at least partially blocked by a tumor, by plaque, or both. An at least partially blocked lumen may be reopened or reinforced with an implantable stent.

[0005] A stent is typically a tubular body that is placed in a lumen in the body. A stent may be delivered inside the body by a catheter that supports the stent in a reduced size configuration as the stent is delivered to a desired deployment site within the body. At the deployment site, the stent may be expanded so that, for example, the stent contacts the walls of the lumen to expand the lumen.

[0006] Advancement of the stent through the body may be monitored during deployment. After the stent is delivered to the target site, the stent can be monitored to determine whether the placement thereof is correct and/or the stent is functioning properly. Methods of tracking and monitoring stent after delivery include X-ray fluoroscopy and magnetic resonance imaging (“MRI”).

[0007] Stents made from tantalum alloys have been identified as being easily detectable using X-ray fluoroscopy and MRI because of the high density of tantalum. Furthermore, tantalum alloys are typically compatible with MRI techniques because they do not produce substantial amounts of magnetic artifacts and/or image distortions or voids during MRI imaging. Additionally, tantalum alloys have proven to be biocompatible and corrosion resistant.

SUMMARY

[0008] Articles such as stents are typically fabricated by laser cutting a selected pattern into a length of metal tubing. Following laser cutting, islands (i.e., the cut-out sections between the struts and other structural features) may be stuck in between the struts and other features of the laser cut pattern for a variety of reasons. The present disclosure includes methods for removing islands from laser cut articles using a chemical etching solution to remove material in the strut-island gap. The methods disclosed herein may optionally include application of heat and/or ultrasonic agitation to increase the chemical activity of the chemical etching solution and to vibrate the islands out of position. The etching methods described here can be used to effectively remove islands from laser cut articles with no structural damage and no operator dependency.

[0009] In one embodiment, a method for removing an island from a laser cut article is disclosed. The method includes steps of (1) providing a refractory metal workpiece having an outer surface and an inner surface, (2) laser cutting the refractory metal workpiece substantially continuously along a laser cut line that extends from the outer surface to the inner surface to produce an article that includes a plurality of laser cuts and one or more islands remaining between the laser cuts, and (3) chemically treating the article to remove the one or more islands therefrom so as to form an implantable device. Typically, the islands may be affixed to the laser cut article with one or more of slag, remelt, laser-ablated material, oxide-oxide bonding; or the islands may be affixed to the laser cut article by geometric constraints. According to one embodiment, the refractory metal workpiece is made from a material selected from the group consisting of tantalum, niobium, tungsten, and alloys thereof. According to another embodiment, the implantable device is an implantable refractory metal stent.

[0010] In one embodiment, the chemical treating step further includes disposing the article in a chemical etching solution that includes hydrofluoric acid (HF), nitric acid (HNO₃), and, optionally, urea. Optionally, the chemical treating step can further include agitating the article in the chemical etching solution and/or heating the article in the chemical etching solution to a temperature in a range from about 40°C to about 70°C while the article is disposed in the chemical etching solution.

[0011] In another embodiment, a method for removing an island from a refractory metal article is disclosed. The method includes steps of (1) providing a refractory metal workpiece having an outer surface and an inner surface, (2) laser cutting the refractory metal workpiece substantially continuously along a laser cut line that extends from the outer surface to the inner surface in a single pass to produce a laser cut refractory metal article that includes a plurality of laser cuts and one or more islands remaining between the laser cuts, and (3) treating the laser cut refractory metal article to remove the one or more islands therefrom. The treating includes disposing the laser cut refractory metal article in a chemical etching solution that includes HF, HNO₃, and, optionally, urea for a period of time sufficient to remove the one or more islands therefrom so as to form an implantable device.

[0012] In yet another embodiment, a method for removing an island from an implantable article is disclosed. The method includes steps of (1) providing a tubular tantalum alloy workpiece having an outer surface and an inner surface, (2) laser cutting the tubular tantalum alloy workpiece substantially continuously along a patterned laser cut line that extends from the outer surface to the inner surface to produce a laser cut stent that includes a patterned plurality of laser cut struts and one or more islands remaining between the laser cut struts, wherein the laser cut struts have a cross-sectional dimension of about 40 μm to about 120 μm, (3) treating the laser cut refractory metal stent to remove the one or more islands therefrom, and (4) treating the laser cut refractory metal stent in the etching solution under heating and sonication for a period of time sufficient to remove the one or more islands therefrom so as to form an implantable stent. The treating includes (i) disposing the laser cut refractory metal stent in a chemical etching solution that includes HF, HNO₃, and, optionally, urea, (ii) heating the laser cut refractory metal stent in the chemical etching solution to a temperature in a range from about 40°C to about 70°C, (iii) sonating the laser cut refractory metal stent in the chemical etching solution using an ultrasonic apparatus. The treating does not include use of a mask capable of defining a plurality of struts and a plurality of islands remaining between the struts.

[0013] In still another embodiment, a method of manufacturing an implantable article includes (1) providing a first refractory metal workpiece having an outer surface and an inner surface, the first refractory metal workpiece being made from a material selected from the group consisting of tantalum, niobium, tungsten, zirconium, molybdenum, and alloys
thereof, (2) laser cutting the refractory metal workpiece in a single pass using a picosecond laser apparatus substantially continuously along a patterned laser cut line that extends from the outer surface to the inner surface to form a laser cut stent that includes a patterned plurality of laser cut struts and one or more islands remaining between the laser cut struts, wherein the laser cut struts have a cross-sectional dimension of about 40 μm to about 120 μm, (3) treating the laser cut refractory metal stent to remove the one or more islands therefrom, (4) treating the laser cut refractory metal stent in the etching solution under sonication and heating for a period of time sufficient to remove the one or more islands therefrom so as to form an implantable stent, (5) electropolishing the laser cut refractory metal stent in an electropolishing solution, and (6) heat treating the laser cut refractory metal stent so as to form an implantable stent. The treating includes (i) disposing the laser cut refractory metal stent in a chemical etching solution that includes HF, HNO₃, and, optionally, urea, (ii) heating the laser cut refractory metal stent in the chemical etching solution to a temperature in a range from about 40°C to about 70°C, (iii) sonication the laser cut refractory metal stent in the chemical etching solution using an ultrasonic apparatus.

These and other objects and features of the present invention will become more fully apparent from the following description and appended claims, or may be learned by the practice of embodiment of the invention as set forth hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

To further clarify the above and other advantages and features of the present invention, a more particular description of the invention will be rendered by reference to specific embodiments thereof which are illustrated in the appended drawings. It is appreciated that these drawings depict only illustrated embodiments of the invention and are therefore not to be considered limiting of its scope. The invention will be described and explained with additional specificity and detail through the use of the accompanying drawings in which:

FIG. 1A schematically illustrates a laser cut stent having islands intact;

FIG. 1B illustrates an enlarged view of the stent of FIG. 1A;

FIG. 2A schematically illustrates an isometric view of a laser cut stent similar to the stent depicted in FIG. 1A with the islands having been removed according to one or more of the methods described herein;

FIG. 2B illustrates an enlarged view of the stent of FIG. 2A;

FIG. 3 is a photomicrograph of a laser cut stent showing a cleaned surface and intact islands;

FIG. 4 is an electron micrograph of the interior diameter of a laser cut stent with intact islands;

FIG. 5 is an electron micrograph of a laser cut stent showing a cross-section of individual laser cuts;

FIG. 6 is a flow diagram illustrating a method for removing an island from a laser cut article;

FIG. 7 is a flow diagram illustrating a method for removing an island from a laser cut article;

FIG. 8 is a flow diagram illustrating a method for removing an island from a laser cut article;

FIG. 9 is a flow diagram illustrating a method for manufacturing a laser cut stent;

FIG. 10 is a flow diagram illustrating another method for manufacturing a laser cut stent; and

FIG. 11 illustrates a device adapted for supporting a plurality of laser cut articles during a procedure for removing one or more islands.

DETAILED DESCRIPTION

Articles such as stents are typically fabricated by laser cutting a selected pattern into a length of metal tubing. Following laser cutting, islands (i.e., the cut out sections between the struts and other structural features) may be stuck in between the struts and other features of the laser cut pattern for a variety of reasons. The present disclosure includes methods for removing islands from laser cut articles using a chemical etching solution to remove material in the strut-island gap. The methods disclosed herein may optionally include application of heat and/or ultrasonic agitation to increase the chemical activity of the chemical etching solution and to vibrate the islands out of position. The etching methods described here can be used to effectively remove islands from laser cut articles with no structural damage and no operator dependency. And while the description that follows refers to stents and other implantable articles, one will appreciate that the methods and apparatuses described herein can be applied to essentially any metal laser cut article.

I. Stents

Referencing now to FIGS. 1A and 1B, an exemplary laser cut stent 100 having intact islands 112 is illustrated. Laser cut stent 100 is fabricated by laser cutting a selected stent pattern into a metal tube. The laser cuts extend all the way from the outer surface of the tube through the inner surface of the tube. In the illustrated embodiment, the laser cut stent 100 appears to have a solid outer wall with a series of patterned cuts in the tube. That is, the cut-out material tends to stay in the tube even after laser cutting.

The stent 100 in the illustrated embodiment includes a number of structural elements such as struts 104, bends 106, and connector elements 108. The regions of waste material left in between the structural elements after the laser cutting process are referred to as islands 112. The islands 112 need to be removed in order to convert the laser cut stent 100 into an implantable stent such as stent 200 shown in FIG. 2. Each island 112 in the illustrated embodiment further includes a series of circular cuts 114 joined by linear cuts 116 and 118 that are positioned in the islands 112 to facilitate removal of the islands 112.

Laser cut stent 100 is made up of a number of ring structures 102 that are coupled together lengthwise. The ring structures 102 are in turn made up of a number of strut elements 104 that are joined together by bends 106. Individual rings (e.g., rings 102a and 102b) are interconnected longitudinally one to another by a number of connector elements 108 that connect a subset of the bends 106 to the illustrated double bend structures 110a and 110b. In the illustrated example, the strut elements 104, bends 106, connector elements 108, and the other structural elements have a square or slightly rectangular profile with dimensions of about 70μm to about 150 μm on a side.

The illustrated stent 100 is fabricated by laser cutting the desired pattern of struts 104, bends 106, and connectors 108 into a length of metal tubing. Stents such as stent 100 are typically laser cut out of metal tubes formed from metals
such as, but not limited to, nickel-titanium, cobalt-chromium, stainless steel, and refractory metals such as tantalum and tantalum alloys. When the desired stent pattern is cut, the material between the patterned cuts (i.e., the islands 112) typically stays attached to the tube. In many respects, the laser cut stent 100 with attached islands 112 resembles a solid tube having a series of patterned lines cut into the tube. This is illustrated by the line drawings in FIGS. 1A and 1B and in the photomicrographs shown in FIGS. 3 and 4.

[0034] The islands 112 can stay attached to the laser cut stent 100 by a number of possible mechanisms. For example, the islands 112 can be affixed to the stent 100 by slag, remelt, or oxide-oxide bonding left by the laser cutting process. The laser cutting process also results in the re-deposition of laser ablated material into the gap between the laser cut features (e.g., struts 104, bends 106, and connectors 108) and the islands 112.

[0035] Even in the absence of slag, remelt, oxide-oxide bonding, or deposited laser ablated material, the islands 112 may be geometrically constrained from falling out of the laser cut tube by the physical dimensions of the tube and the cuts and/or because of changes that can occur as a result of the laser cutting process. In the present case, for example, blank tubes for stent fabrication are only about 1.5 mm to about 5 mm in diameter and the material is only about 50 μm to about 110 μm thick. In turn, the kerf from the laser used to cut the stent pattern is only about 10 μm to about 15 μm on the outer diameter of the tube and about 2 μm to about 4 μm on the inner diameter. This is illustrated in FIGS. 4 and 5. FIG. 4 is an electron micrograph of a stent-patterned laser cut tube 400 at approximately 60x magnification. Given that the tube 400 is only about 1.5 mm in diameter, one can readily appreciate the precision of the laser cuts 402 that are visible on the interior of a laser cut tube 400. One can also see that the laser cuts 402 extend all the way through the tube 400. FIG. 5 is an electron micrograph of a cross-section 502 of a laser cut tube 500 at approximately 600x magnification. FIG. 5 illustrates the size difference of the laser cut kerf on the outer diameter 504 and the inner diameter 506 of the laser cut tube 500. As mentioned above, the laser kerf is only about 10 μm to about 15 μm on the outer diameter 504 of the tube 500 and about 2 μm to about 4 μm on the inner diameter 506, which leaves relatively little space for the islands to fall out on their own. In another example, the act of laser cutting the tube may have the effect of relieving stress in the tube, which can cause the material to expand slightly or twist slightly, essentially locking the islands 112 in place.

[0036] The island removal methods disclosed herein are an alternative to traditional island removal techniques (e.g., “flicking”), which can damage delicate laser cut articles. The refractory metal materials (e.g., tantalum alloys) discussed herein are durable, biocompatible, and radiopaque. Refractory metal tubes can be laser cut to produce stents having struts with an as-cut cross-sectional dimension of about 80 μm and finished dimensions of about 50 μm to about 65 μm. Nevertheless, the thin struts and other structural elements like those shown in the illustrated examples are quite fragile and are therefore easily distorted, which disfavors the use of flicking and other traditional techniques for island removal.

[0037] Also, as explained above, the laser cutting process leaves a very small kerf that leaves very little room for the islands to fall out on their own. Traditionally, island removal can be facilitated by using multiple passes with the laser, which widens the kerf. For example, some stent designs and materials can tolerate up to 6 or 7 passes through the laser cutting apparatus, which generally makes the islands fall out on their own or with minimal flicking. In addition, it is possible to increase the size of the laser kerf by increasing the laser power or increasing the gas pressure in the laser. However, these processes can increase the size of the heat-affected zone and can present dimensional difficulties in terms of tolerances of the strut widths and crest radii, since you are depending on the laser’s mechanical controls to ensure the laser is cutting essentially the exact same location on each laser pass. In addition, the laser cutting process can cause dimensional changes in the tube that can essentially wedge the islands in the tube. The effectiveness of traditional island removal techniques such as flicking also depends to a large extent on operator skill. For these reasons and others, traditional island removal techniques are not applicable to the laser cut articles discussed herein.

[0038] Referring now to FIGS. 2A and 2B, a stent 200 is shown. Stent 200 is similar to the stent 100 depicted in FIGS. 1A and 1B except the islands 112 have been removed. Stent 200 is made up of a number of ring structures 102 that include strut elements 104 that are joined together by bends 106. Individual rings (e.g., rings 102a and 102b) are interconnected one to another by a number of connector elements 108 that connect a subset of the bends 106a to the illustrated double bend structures 110a and 110b. Removal of the islands 112 according to the methods disclosed herein produces a stent 200 with an open, expandable structure that is well-suited to, for example, scaffolding a blood vessel.

Li. Methods for Island Removal

[0039] The methods described herein relate to methods for removing an island from a laser cut article (e.g., a stent) using chemical etching solution to remove material in the struts island gap. The methods disclosed herein may optionally include application of heat and/or ultrasonic agitation to increase the chemical activity of the chemical etching solution and to vibrate the islands out of position. The island removal methods disclosed herein are an alternative to traditional island removal techniques (e.g., “flicking”), which can damage delicate laser cut articles and which are not particularly effective with the laser cut articles discussed herein.

[0040] Referring now to FIG. 6, a flow diagram illustrating an embodiment of a general method 600 for removing one or more islands from a laser cut article is shown. The method 600 includes act 610 of disposing a laser cut article in a chemical etching solution and an act 620 of etching the laser cut article to remove one or more islands therefrom. In one embodiment, the laser cut article may be etched in act 620 for about 10 to 60 minutes or about 15 to 30 minutes. In actual practice, however, the etching time necessary to remove the islands from the laser cut article may be affected by parameters such as, but not limited to, the concentration of the etchant, type of acid in the etchant, the size of the kerf, the temperature of the etchant, presence or absence of stirring/agitation of the etchant, and combinations thereof.

[0041] In one embodiment, the laser cut article etched in act 610 can be made from essentially any known metal or metal alloy. For example, the article can be made from steel, a stainless steel such as, but not limited to, 316L stainless steel, a nickel-titanium alloy such as, but not limited to, a binary Ni—Ti alloy, a cobalt chromium alloy such as, but not limited to, L605 cobalt chromium, a platinum chromium alloy, palladium-containing alloys, molybdenum-containing alloys, a
cobalt super alloy, a refractory metal, or a refractory metal alloy such as, but not limited to, a tantalum alloy, and the like.

Referring now to FIG. 11 a device 1100 that can be used to dispose an article (e.g., stent 1160) in a chemical etching solution is illustrated. The device 1100 includes a handle 1110 that can be used to lower or raise the device 1100 into or out of a chemical etching solution, a plurality of supports 1120 that can be used to support one or more laser cut articles (e.g., stents 1160), a support base 1130 that includes cut-outs 1140 for allowing flow of the chemical etchant around the device 1100, and a plurality of support legs 1150. Because of the corrosivity of the chemical etchant, it is preferred that the device 1100 be made from an inert material. Suitable examples of inert materials include, but are not limited to, plastics such as polyethylene and polytetrafluoroethylene (PTFE, Teflon).

In one embodiment, the etching solution employed in act 610 or any of the other methods disclosed herein includes at least one mineral acid. A mineral acid is an inorganic acid derived from one or more inorganic compounds. All mineral acids release hydrogen ions when dissolved in water. Suitable examples of mineral acids include, but are not limited to, hydrochloric acid (HCl), nitric acid (HNO₃), phosphoric acid (H₃PO₄), sulfuric acid (H₂SO₄), hydrofluoric acid (HF), and hydrobromic acid (HBr).

Most mineral acids are classified as “strong acids,” meaning that they dissociate completely when they are dissolved in aqueous solution. One notable exception is hydrofluoric acid (HF), which is technically classified as a weak acid. HF is a solution of hydrogen fluoride gas in water. HF is best known to the public for its ability to dissolve glass by reacting with SiO₂, the major component of most glass, to form silicon tetrafluoride gas and hexafluorosilicic acid. HF is also notable for its ability to dissolve chemically resistant metal and semimetal oxides and refractory metals such as, but not limited to, tantalum, niobium, tungsten, and alloys thereof.

In spite of the fact that HF is technically a “weak” acid, working with HF can be extremely dangerous. HF is readily absorbed through the skin where it can react destructively with the calcium in bones and/or the calcium in blood serum. As a result, acute exposure to HF can, for example, require limb amputation in some cases due to HF’s ability to react with and corrode the calcium compounds that form the structure of bone. In other instances, HF exposure can even cause cardiac arrest through the depletion of serum calcium levels due to the formation of insoluble calcium fluoride.

In one embodiment, the mineral acid in the chemical etching solution employed in act 610 includes at least hydrofluoric acid (HF). In another embodiment, the chemical etching solution employed in act 610 includes hydrofluoric acid (HF) and nitric acid (HNO₃). In yet another embodiment, the chemical etching solution employed in act 610 includes about 1% HF by volume to about 10% HF by volume, about 10% HNO₃ by volume to about 50% HNO₃ by volume, and water, or preferably about 1% HF by volume to about 5% HF by volume, about 10% HNO₃ by volume to about 20% HNO₃ by volume, about 20% HNO₃ by volume to about 45% HNO₃ by volume, about 45% HNO₃ by volume to about 60% HNO₃ by volume, about 60% HNO₃ by volume to about 75% HNO₃ by volume, about 75% HNO₃ by volume to about 85% HNO₃ by volume, about 85% HNO₃ by volume to about 90% HNO₃ by volume, about 90% HNO₃ by volume to about 95% HNO₃ by volume, about 95% HNO₃ by volume to about 98% HNO₃ by volume, about 98% HNO₃ by volume to about 99% HNO₃ by volume, about 99% HNO₃ by volume to about 99.5% HNO₃ by volume, and water.

In still yet another embodiment, the chemical etching solution employed in act 610 includes about 1% HF by volume to about 10% HF by volume, about 10% HNO₃ by volume to about 50% HNO₃ by volume, about 0.5 weight % to about 2 weight % urea, and water, or preferably about 1% HF by volume to about 5% HF by volume, about 20% HNO₃ by volume to about 45% HNO₃ by volume, about 0.8 weight % to about 1.5 weight % urea, and water, or more preferably about 2% HF by volume to about 4% HF by volume, about 25% HNO₃ by volume to about 35% HNO₃ by volume, about 0.9 weight % to about 1.3 weight % urea, and water. Without being tied to one theory, it is believed that the addition of urea to the chemical etching solution may help to stabilize the solution and to increase its longevity (i.e., increase the number of articles that can be etched before having to change the solution). Weight and volume percentages for an etching solution containing about 2% HF by volume to about 4% HF by volume, about 25% HNO₃ by volume to about 35% HNO₃ by volume, about 0.9 weight % to about 1.3 weight % urea, and water are shown below in Table 1.

### TABLE 1

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight %</th>
<th>Low Range</th>
<th>High Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td>25-35%</td>
<td>25%</td>
<td>18.9%</td>
</tr>
<tr>
<td>HF</td>
<td>2-4%</td>
<td>2%</td>
<td>1.84%</td>
</tr>
<tr>
<td>H₂O</td>
<td>56-76%</td>
<td>72.1%</td>
<td>79.2%</td>
</tr>
<tr>
<td>Urea</td>
<td>0.9-1.3%</td>
<td>0.9%</td>
<td>1.0%</td>
</tr>
</tbody>
</table>

Referring now to FIG. 7, another flow diagram illustrating a method 700 for removing an island from a laser cut piece is shown. The method 700 includes an act 710 of providing a first refractory metal article that includes a plurality of laser cuts and one or more islands remaining between the laser cuts and an act 720 of chemically treating the article to remove the one or more islands therefrom so as to form an implantable device.

In one embodiment, the article provided in act 710 is made from a material selected from the group consisting of tantalum, niobium, tungsten, and alloys thereof. Suitable examples of refractory metals employed in any of the methods discussed herein include, but are not limited to, tantalum, niobium, tungsten, and alloys thereof. It has been found that a tantalum alloy that includes tantalum, niobium, and at least one additional element selected from the group consisting of tungsten, zirconium, molybdenum, and/or at least one of hafnium, rhenium, and cerium can fulfill the mechanical and biocompatibility requirements needed for functioning as a medical device.

In one embodiment, the refractory metal articles disclosed herein can be made from an alloy including (a) about 0.1 weight percent to about 70 weight percent niobium, (b) about 0.1 weight percent to about 30 weight percent of at least one element selected from the group consisting of tungsten, zirconium, and molybdenum, (c) up to 5 weight percent of at least one element selected from the group consisting of hafnium, rhenium, and cerium, and (d) tantalum.

In one embodiment, the refractory metal articles disclosed herein can be made from a tantalum alloy that includes a tantalum content of about 78 weight-percent (“wt %”) to about 91 wt %, a niobium content of about 7 wt % to about 12 wt %, and a tungsten content of about 1 wt % to about 10 wt %. However, the tantalum alloy may also include other alloying elements, such as one or more grain-refining elements in an amount up to about 5 wt % of the tantalum alloy.

For example, the one or more grain-refining elements may include at least one of hafnium, cerium, or rhenium.
Tungsten is provided to solid-solution strengthen tantalum, and niobium is provided to improve the ability of tantalum to be drawn. The tantalum alloy is a substantially single-phase, solid-solution alloy having a body-centered cubic crystal structure. However, some secondary phases may be present in small amounts (e.g., inclusions) depending upon the processing employed to fabricate the tantalum alloy.

The composition of the tantalum alloy may be selected from a number of alloy compositions according to various embodiments. In an embodiment, the niobium content is about 9 wt % to about 10.5 wt %, the tungsten content is about 6.0 wt % to about 8 wt %, and the balance may include tantalum (e.g., the tantalum content being about 80 wt % to about 85 wt %) and, if present, other minor alloying elements and/or impurities. In a more detailed embodiment, the niobium content is about 10 wt %, the tungsten content is about 7.5 wt %, and the balance may include tantalum (e.g., the tantalum content being about 82.5 wt %) and, if present, other minor alloying elements and/or impurities. In another more detailed embodiment, the niobium content is about 10 wt %, the tungsten content is about 7.5 wt %, and the balance may include tantalum (e.g., the tantalum content being about 87.5 wt %) and, if present, other minor alloying elements and/or impurities.

In another embodiment, the niobium content is about 10.5 wt % to about 13 wt %, the tungsten content is about 5.0 wt % to about 6 wt %, and the balance may include tantalum (e.g., the tantalum content being about 80 wt % to about 82 wt %) and, if present, other minor alloying elements and/or impurities. In a more detailed embodiment, the niobium content is about 12.5 wt %, the tungsten content is about 5.8 wt %, and the balance may include tantalum (e.g., the tantalum content being about 81 wt % to about 81.5 wt %) and, if present, other minor alloying elements and/or impurities.

In a specific example, the tantalum-containing refractory metal article disclosed herein may be made from a tantalum alloy that includes about 82.5 weight percent tantalum, about 10 weight percent niobium, and about 7.5 weight percent tungsten.

In another specific example, the tantalum-containing refractory metal article disclosed herein may be made from a tantalum alloy that includes about 87.5 weight percent tantalum, about 10 weight percent niobium, and about 2.5 weight percent tungsten.

In an embodiment, the refractory metal (e.g., a tantalum alloy) may exhibit a grain microstructure including recrystallized, generally equiaxed grains characteristic of being formed by heat treating a precursor product or a stent body itself, both of which may be severely plastically deformed in a drawing process. Depending upon the extent of recrystallization process, the grain microstructure may be only partially recrystallized. In some embodiments, the recrystallization process may substantially completely recrystallize the grain microstructure with the new recrystallized grains having consumed substantially all of the old deformed grains. Even when the grain microstructure is partially recrystallized, it will be apparent from microstructural analysis using optical and/or electron microscopy that the grain microstructure includes some recrystallized grains having, for example, a generally equiaxed geometry. An average grain size of the tantalum alloy may be about 10 μm to about 20 μm and, more particularly, about 13 μm to about 16 μm depending on the extent of recrystallization and the amount of the optional one or more grain-refining alloy elements in the tantalum alloy.

In other embodiments, the refractory metal alloy may be stress relieved at a temperature below a recrystallization temperature of the tantalum alloy so that the grain microstructure is relatively unchanged from the as-drawn condition. Thus, in the stress-relieved condition, the grain microstructure may include essentially only non-equiaxed, deformed, cold-worked grains. However, the stress-relief heat treatment may at least partially remove at least one of hydrogen, oxygen, or oxygen from the tantalum alloy, which can detrimentally embrittle the tantalum alloy. Thus, the tantalum alloy in the stress-relieved condition may exhibit an improved ductility relative to the as-drawn condition, while the tensile yield strength and tensile ultimate tensile strength are generally unaffected by the stress-relief heat treatment.

The heat-treated refractory metal alloy from which the stent body is made may exhibit combination of strength (e.g., tensile yield strength and ultimate tensile strength) and ductility (e.g., percent elongation) suitable to withstand loading conditions encountered when implanted and utilized in a lumen of a living subject. The tensile yield strength may be the 0.2% offset yield strength determined in a uniaxial tensile test when no yield point is present, and the yield point if the tantalum alloy exhibits a yield point. For example, the tantalum alloy may exhibit a tensile elongation of about 0% to about 40%, a tensile yield strength of about 400 MPa to about 815 MPa, and an ultimate tensile strength of about 500 MPa to about 850 MPa as determined by, for example, tensile testing a tubular body from which the stent body may be cut from or a drawn wire in a uniaxial tensile test. In an embodiment, the tantalum alloy (e.g., about 82.5 wt % tantalum, about 10 wt % niobium, and about 7.5 wt % tungsten) may exhibit a tensile elongation of about 9% to about 40%, a tensile yield strength of about 455 MPa to about 810 MPa, and an ultimate tensile strength of about 515 MPa to about 850 MPa. In another embodiment, the tantalum alloy may exhibit a tensile elongation of about 10% to about 25%, a tensile yield strength of about 400 MPa to about 500 MPa, and an ultimate tensile strength of about 500 MPa to about 550 MPa. In one embodiment, the tantalum alloy may exhibit a tensile elongation of about 20% to about 23%, a tensile yield strength of about 450 MPa to about 500 MPa, and an ultimate tensile strength of about 500 MPa to about 550 MPa.

In an embodiment, a heat-treated refractory metal alloy from which the stent body is made having a tantalum content of about 87.5 wt %, a niobium content of about 10 wt %, and a tungsten content of about 2.5 wt % and an at least partially recrystallized grain microstructure may exhibit a tensile elongation of about 9% to about 40%, a tensile yield strength of about 400 MPa to about 800 MPa, and an ultimate tensile strength of about 500 MPa to about 850 MPa. In one embodiment, the heat-treated tantalum alloy may exhibit a tensile elongation of about 10% to about 25%, a tensile yield strength of about 400 MPa to about 500 MPa, and an ultimate tensile strength of about 500 MPa to about 550 MPa.

In an embodiment, a stress-relieved refractory metal alloy from which the stent body is made having a tantalum content of about 82.5 wt %, a niobium content of about 10 wt %, and a tungsten content of about 7.5 wt % may exhibit a percent elongation of about 9% to about 15% (e.g., about 10% to about 11%), a tensile yield strength of about 650 MPa to about 850 MPa, and an ultimate tensile strength of about 700
MPa to about 850 MPa. In the stress-relieved condition, the percent elongation of the tantalum alloy may increase by at least about 100%, at least about 200%, at least about 300%, or about 200% to about 300% compared to the same tantalum alloy in the as-drawn (i.e., un-stress-relieved condition), while the tensile yield strength and ultimate tensile strength are reduced. As yield strength and ultimate tensile strength go down, the ductility of the tantalum alloy tends to increase. The reduction in tensile yield strength and ultimate tensile strength and the increase in ductility needs to be balanced, but, in general, increasing ductility tends to yield a more durable medical device fabricated from the tantalum alloy. For example, an alloy having increased ductility is less likely to crack when radially stressed. The grain microstructure may also be relatively un-changed from the as-drawn condition and may include deformed, non-equiaxed grains.

Suitable examples of implantable articles fabricated in act 720 include, but are not limited to, medical implants and devices including minimal-invasive devices, such as, guide wires, intra-cavernous implants, in particular intra-esophagus, intra-urethra, intra-tracheal implants and intra-vascular implants, in particular stents, stent grafts, stent graft connector, heart valve repair device, or filters.

Referring now to FIG. 8, yet another flow diagram illustrating a method 800 for removing an island from a laser cut stent is shown. The method 800 includes an act 810 of providing a laser cut refractory metal stent that includes a patterned plurality of laser cut struts and one or more islands remaining between the laser cut struts and an act 820 of disposing the laser cut refractory metal stent in a chemical etching solution that includes hydrofluoric acid (HF) nitric acid (HNO<sub>3</sub>), and, optionally, urea, as described in greater detail above. The method 800 further includes an act 830 of heating the laser cut refractory metal stent in the chemical etching solution to a temperature in a range from about 40° C. to about 70° C., an act 840 of sonicating the laser cut refractory metal stent in the chemical etching solution using an ultrasonic apparatus, and an act 850 of treating the laser cut refractory metal stent in the etching solution under heating and sonicating for a period of time sufficient to remove the one or more islands therefrom so as to form an implantable stent.
ration of Danbury, Conn. USA. The Branson 2510 is an ultrasonic cleaning unit that operates at a frequency of 40 kHz and that includes a temperature controlled bath. In operation, a beaker or another vessel containing the etching solution and the laser cut articles can be disposed in the ultrasonic bath. The beaker containing the laser cut articles can be left in the ultrasonic bath under heating and sonicating for a period of time sufficient to remove the one or more islands therefrom so as to form an implantable stent.

[0071] In one embodiment, the period of time in the etching solution sufficient to remove the islands from the laser cut article is in a range from about 5 minutes to about 90 minutes, or about 10 minutes to about 60 minutes, or about 15 minutes to about 30 minutes. One will appreciate, however, that the actual time needed may be affected by factors such as the size of the laser cut kerf(s) in the article, the temperature, sonication, concentration and composition of the acids in the etching solution, and the like.

[0072] Referring now to FIG. 9, still yet another flow diagram illustrating an embodiment of a method 900 for manufacturing an implantable article is illustrated. The method 900 includes an act 910 of providing a first refractory metal workpiece, the first refractory metal workpiece being made from a material selected from the group consisting of tantalum, niobium, tungsten, zirconium, molybdenum, and alloys thereof and an act 920 of laser cutting the first refractory metal workpiece to form a laser cut refractory metal stent that includes a patterned plurality of laser cut struts and one or more islands remaining between the laser cut struts. Method 900 further includes an act 930 of disposing the laser cut refractory metal stent in a chemical etching solution that includes hydrofluoric acid (HF) nitric acid (HNO₃) and, optionally, urea, an act 940 of heating the laser cut refractory metal stent in the chemical etching solution to a temperature in a range from about 40°C to about 70°C, an act 950 of sonicating the laser cut refractory metal stent in the chemical etching solution using an ultrasonic apparatus, and an act 960 of treating the laser cut refractory metal stent in the etching solution under heating and sonicating for a period of time sufficient to remove the one or more islands therefrom so as to form an implantable stent, as described in greater detail above.

[0073] Method 900 further includes an act 970 of chemically treating and/or heat treating the refractory metal stent to produce a substantially defect-free surface finish and improve the performance characteristics of the stent. For example, the heat treating may be used to modify one or more mechanical properties of the stent, such as, but not limited to, an increase in yield strength, tensile strength, flexibility, toughness, and the like.

[0074] According to the method 900 illustrated in FIG. 9, the method of manufacturing a refractory metal stent further includes an act 970 of chemically treating and/or heat treating the refractory metal stent to produce a substantially defect-free surface finish and improve the performance characteristics of the stent. For example, the heat treating may be used to modify one or more mechanical properties of the stent, such as, but not limited to, an increase in yield strength, tensile strength, flexibility, toughness, and the like.

[0075] Referring now to FIG. 10, still yet another flow diagram illustrating a method 1000 for manufacturing an implantable article is illustrated. The method 1000 includes an act 1010 of providing a first refractory metal workpiece, the first refractory metal workpiece being made from a material selected from the group consisting of tantalum, niobium, tungsten, zirconium, molybdenum, and alloys thereof, an act 1020 of laser cutting the first refractory metal workpiece to form a laser cut refractory metal stent that includes a patterned plurality of laser cut struts and one or more islands remaining between the laser cut struts, an act 1030 of disposing the laser cut refractory metal stent in a chemical etching solution that includes hydrofluoric acid (HF) nitric acid (HNO₃), and, optionally, urea, an act 1040 of heating the laser cut refractory metal stent in the chemical etching solution to a temperature in a range from about 40°C to about 70°C, an act 1050 of sonicating the laser cut refractory metal stent in the chemical etching solution using an ultrasonic apparatus, and an act 1060 of treating the laser cut refractory metal stent in the etching solution under heating and sonicating for a period of time sufficient to remove the one or more islands therefrom so as to form an implantable stent, as described in greater detail above.

[0076] The method 1000 of manufacturing a refractory metal stent further includes an act 1070 of rinsing, drying, and inspecting the laser cut and implant free stent. For instance, the act 1070 of rinsing, drying, and inspecting can include at least three rinses in deionized water (either with or without sonication), a rinse in alcohol such as methanol, ethanol, or isopropanol, and drying the stent with compressed air.

[0077] The method 1000 further includes an act 1080 of electropolishing the laser cut refractory metal stent in an electropolishing solution to produce a substantially defect free finish on the stent, and an act 1090 of heat treating the laser-cut refractory metal stent so as to form an implantable stent.

[0078] The present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

What is claimed is:

1. A method for removing an island from a laser cut article, comprising:
   providing a refractory metal workpiece having an outer surface and an inner surface;
   laser cutting the refractory metal workpiece substantially continuously along a laser cut line that extends from the outer surface to the inner surface to produce an article that includes a plurality of laser cuts and one or more islands remaining between the laser cuts; and
   chemically treating the article to remove the one or more islands therefrom so as to form an implantable device.

2. The method of claim 1 wherein the laser cutting is performed in a single pass.

3. The method of claim 1 wherein the one or more islands are affixed to the article by one or more of slag, remelt, laser ablated material, oxide-oxide bonding, or geometric constraints.

4. The method of claim 1 wherein the refractory metal workpiece is made from a material selected from the group consisting of tantalum, niobium, tungsten, and alloys thereof.

5. The method of claim 1 wherein the implantable device is an implantable refractory metal stent.

6. The method of claim 1, the chemically treating further comprising disposing the article in a chemical etching solution that includes hydrofluoric acid (HF) and nitric acid (HNO₃).

7. The method of claim 6, further comprising disposing the article in the chemical etching solution for a period of time in a range from about 10 minutes to about 60 minutes.
8. The method of claim 6, further comprising: sonicating in the chemical etching solution using an ultrasonic cleaning apparatus while the article is disposed in the chemical etching solution; and heating the article in the chemical etching solution to a temperature in a range from about 40° C. to about 70° C. while the article is disposed in the chemical etching solution.

9. The method of claim 1, the chemically treating further comprising etching the article in a chemical etching solution including at least one mineral acid.

10. The method of claim 9, the at least one mineral acid including hydrofluoric acid (HF).

11. The method of claim 9, the at least one mineral acid including hydrofluoric acid (HF) and nitric acid (HNO₃).

12. The method claim 11, the chemical etching solution including about 1% HF by volume to about 10% HF by volume, about 10% HNO₃ by volume to about 50% HNO₃ by volume, and water.

13. The method claim 11, the chemical etching solution including about 1% HF by volume to about 3% HF by volume, about 20% HNO₃ by volume to about 45% HNO₃ by volume, and water.

14. The method claim 11, the chemical etching solution including about 1% HF by volume to about 3% HF by volume, about 25% HNO₃ by volume to about 35% HNO₃ by volume, and water.

15. The method claim 11, wherein the chemical etching solution further includes urea.

16. The method claim 11, the chemical etching solution including about 2% HF by volume to about 4% HF by volume, about 25% HNO₃ by volume to about 35% HNO₃ by volume, about 0.9 weight % (“wt %”) to about 1.3 wt % urea, and water.

17. A method for removing an island from a refractory metal article, the method comprising:

- providing a refractory metal workpiece having an outer surface and an inner surface;
- laser cutting the refractory metal workpiece substantially continuously along a laser cut line that extends from the outer surface to the inner surface in a single pass to produce a laser cut refractory metal article that includes a plurality of laser cuts and one or more islands remaining between the laser cuts; and
- treating the laser cut refractory metal article to remove the one or more islands therefrom, the treating comprising:
  - disposing the laser cut refractory metal article in a chemical etching solution that includes hydrofluoric acid (HF) and nitric acid (HNO₃) for a period of time sufficient to remove the one or more islands therefrom so as to form an implantable device.

18. The method of claim 17, the treating further comprising:

- heating the laser cut refractory metal article in the chemical etching solution to a temperature in a range from about 40° C. to about 70° C.; and
- sonicating the laser cut refractory metal article in the chemical etching solution using an ultrasonic apparatus.

19. The method of claim 18, further comprising treating the laser cut refractory metal article for a period of time in a range from about 10 minutes to about 60 minutes.

20. The method claim 17, wherein the chemical etching solution includes about 1% HF by volume to about 10% HF by volume, about 10% HNO₃ by volume to about 50% HNO₃ by volume, and water.

21. The method of claim 17, wherein the refractory metal workpiece is made from a material selected from the group consisting of tantalum, niobium, tungsten, and alloys thereof.

22. The method of claim 17, wherein the refractory metal workpiece is made from a tantalum alloy, comprising:

- about 75 to about 90 weight percent tantalum;
- about 8 to about 12 weight percent niobium;
- about 2 to about 10 weight percent tungsten.

23. The method of claim 22, wherein the refractory metal workpiece further comprises at least one of zirconium or molybdenum.

24. A method for removing an island from an implantable article, the method comprising:

- providing a tubular tantalum alloy workpiece having an outer surface and an inner surface;
- laser cutting the tubular tantalum alloy workpiece substantially continuously along a patterned laser cut line that extends from the outer surface to the inner surface to produce a laser cut stent that includes a patterned plurality of laser cut struts and one or more islands remaining between the laser cut struts, wherein the laser cut struts have a cross-sectional dimension of about 40 μm to about 120 μm; and
- treating the laser cut stent to remove the one or more islands therefrom, the treating comprising:
  - disposing the laser cut stent in a chemical etching solution that includes hydrofluoric acid (HF) and nitric acid (HNO₃);
  - heating the laser cut stent in the chemical etching solution to a temperature in a range from about 40° C. to about 70° C.; and
  - sonicating the laser cut stent in the chemical etching solution using an ultrasonic apparatus; and
- treating the laser cut stent in the chemical etching solution under heating and sonication for a period of time sufficient to remove the one or more islands therefrom so as to form an implantable stent.

25. The method of claim 24, wherein the laser cutting is performed in a single pass using a picosecond laser apparatus.

26. The method of claim 24, wherein the tubular tantalum alloy workpiece includes tantalum and one or more of niobium, tungsten, zirconium and molybdenum.

27. The method of claim 24, wherein the laser cut struts of the laser cut stent have a cross-sectional dimension of about 45 μm to about 80 μm.

28. The method of claim 24, wherein the laser cut struts of the laser cut stent have a cross-sectional dimension of about 50 μm to about 80 μm.

29. A method of manufacturing an implantable article, comprising:

- providing a first refractory metal workpiece having an outer surface and an inner surface, the first refractory metal workpiece being made from a material selected from the group consisting of tantalum, niobium, tungsten, zirconium, molybdenum, and alloys thereof;
- laser cutting the first refractory metal workpiece in a single pass using a picosecond laser apparatus substantially continuously along a patterned laser cut line that extends from the outer surface to the inner surface to form a laser cut stent that includes a patterned plurality of laser cut
struts and one or more islands remaining between the laser cut struts, wherein the laser cut struts have a cross-sectional dimension of about 40 μm to about 120 μm; treating the laser cut stent for a period of time sufficient to remove the one or more islands therefrom, the treating comprising:

- sonicating the laser cut stent in the chemical etching solution using an ultrasonic apparatus;
- wherein the treating does not include use of a mask capable of defining a plurality of struts and a plurality of islands remaining between the struts;
- electropolishing the laser cut metal stent in an electropolishing solution; and
- heating the laser cut refractory metal stent so as to form an implantable stent.