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(54) **Titanium-containing Article and its method of manufacture**

(57) An article made of an alloy, and a method for making the article, are presented. The alloy is substantially free of martensite, and comprises the following composition: at least about 75 weight percent titanium; up to about 10 weight percent of a beta stabilizing component; from about 3 weight percent to about 15 weight percent of an alpha stabilizing component; and from about 0.05 weight percent to about 5 weight percent germanium.

Another embodiment is a method for fabricating an article. The method comprises providing a billet made of an alloy as described above, and stabilizing the billet microstructure to form a stabilized billet; the method may further comprise superplastically processing the stabilized billet to form a processed item.

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## Description

### BACKGROUND

**[0001]** This invention relates to metal alloys. More particularly, this invention relates to titanium alloys, and to methods for fabricating articles made with titanium alloys.

**[0002]** Titanium alloys are valued for their advantageous properties, including, for example, high strength-to-weight ratio, good resistance to corrosion, and high melting temperature. However, titanium metal is expensive due to the cost-intensive extractive metallurgical processes required to convert titanium ore to usable metal. As a result, the costs of fabrication of articles from titanium and its alloys are exacerbated by material waste inherent in machining processes, such as grinding, that are used to form a titanium item into its final desired shape.

**[0003]** To combat the costs associated with titanium manufacturing, the metalworking industry has developed so-called "near net shape processing" to allow for the forming of an intermediate article, such as a forging or a powder metallurgy product, that requires less removal of material to form the final article. One example of such processes in the metal industry is superplastic processing, which term is used herein to include any forging, forming, or other metalworking method that involves superplastic deformation of a material. Certain metals, such as titanium- and aluminum-based alloys, have the ability under certain conditions of temperature and strain rate to accommodate very high tensile elongation (deformation); as a result, these materials may be processed into more complex shapes than conventional materials, allowing, for example, the fabrication of near net shape forgings with attendant reductions in machining waste relative to conventional forgings.

**[0004]** Although superplastic processing of titanium alloys provides an attractive route for efficient, cost effective manufacturing, it is not without its challenges. Notably, the temperature required for superplastic processing of conventional titanium alloys is relatively high, resulting, for example, in grain growth during processing that may detract from the properties of the final product. Moreover, the high temperature may also require the use of expensive refractory tooling and high amounts of energy to work through the process.

**[0005]** Titanium workpieces having extremely fine grain sizes (and thus a higher fraction of material residing at grain boundaries) compared to conventional materials could be applied to reduce the temperatures needed to achieve superplasticity, because grain boundary sliding is a major mechanism for deformation in these alloys at the temperatures used in forming operations. However, obtaining such a fine grain size, and maintaining the fine grain size during the superplastic processing operation is a difficult challenge, because the heat applied to the workpiece provides a driving force for the grains to grow during processing.

**[0006]** Thus there is a need in the industry for titanium materials that can be processed to form ultrafine grain sizes and to maintain this refined microstructure during superplastic processing operations. There is also a need for methods to form titanium alloy articles via superplastic processing to provide cost effective, near-net-shape manufacturing.

### BRIEF DESCRIPTION

**[0007]** Embodiments of the present invention are provided to meet these and other needs. One embodiment is an article that comprises an alloy. The alloy is substantially free of martensite, and comprises the following composition: at least about 75 weight percent titanium; up to about 10 weight percent of a beta stabilizing component; from about 3 weight percent to about 15 weight percent of an alpha stabilizing component; and from about 0.05 weight percent to about 5 weight percent germanium.

**[0008]** Another embodiment is a method for fabricating an article. The method comprises providing a billet made of an alloy as described above, and stabilizing the billet microstructure to form a stabilized billet. In some embodiments, the method further comprises superplastically processing the stabilized billet to form a processed item.

### DETAILED DESCRIPTION

**[0009]** It will be appreciated that where materials and articles are described herein as "comprising" or "including" one or more components, the scope of the description includes, without limitation, materials made only of the stated components; materials made of the stated components and including other components that do not materially affect the superplastic behavior of the material; and materials including the stated components but not excluding other components. Moreover, where lists of alternatives are provided, the alternatives are not meant to be exclusive; one or more of the alternatives may be selected, except where otherwise explicitly stated.

**[0010]** In accordance with embodiments of the present invention, an article comprises an alloy with at least about 75 weight percent titanium, and thus may be referred to herein as a "titanium-based alloy," or more simply a "titanium alloy." The article, in some embodiments, is a component of a turbine assembly, such as a stationary gas turbine assembly or an aircraft engine. Examples of such components include, but are not limited to an engine mount, a liner, a heat shield, a gear-box casing, a bladed disk, or a blade. In some embodiments, the article is not a finished component, but is a material for use as feed-stock in some future fabrication process.

**[0011]** Titanium alloys often comprise one or more so-called "beta stabilizers," which are elements that promote the existence of beta-phase titanium (a body-centered cubic phase, referred to herein as "beta-phase" or simply "beta"). Beta phase is known to enhance the formability of titanium alloys. In some embodiments of the present

invention, the alloy includes up to about 10 weight percent of a beta stabilizing component. In particular embodiments, the beta stabilizing component is present at a level in the range from about 3.5 weight percent to about 4.5 weight percent. The beta stabilizing component can itself include one or more beta stabilizers, such as, for example, refractory metals, platinum group metals, and transition metals. Particular examples of beta stabilizers include, but are not limited to, molybdenum, vanadium, tantalum, niobium, manganese, iron, chromium, cobalt, nickel, rhenium, palladium, tungsten, zirconium, and copper. In particular embodiments, the beta stabilizing component may be vanadium, molybdenum, niobium, tantalum, iron, or some combination including one or more of these.

**[0012]** So-called "alpha stabilizers," are elements used in titanium alloys to promote the existence of alpha-phase titanium (a hexagonal close-packed phase, referred to herein as "alpha-phase" or "alpha") recognized for its advantageous strength and toughness. In some embodiments of the present invention, the alloy includes from about 3 weight percent to about 15 weight percent of an alpha stabilizing component. In particular embodiments, the alpha stabilizing component is present at a level in the range from about 5.5 weight percent to about 6.75 weight percent. The alpha stabilizing component can itself include one or more alpha stabilizers, such as, for example, tin, aluminum, gallium, lanthanum, cerium, carbon, oxygen, or nitrogen. In particular embodiments, the alpha stabilizing component may be aluminum, tin, or some combination including one or more of these.

**[0013]** According to embodiments of the present invention, the alloy further includes germanium, from a minimum of about 0.05 weight percent to about 5 weight percent. In some embodiments, the germanium is present in an amount from about 0.05 weight percent to about 1 weight percent, and in particular embodiments the germanium is present in an amount in the range from about 0.05 weight percent to about 0.4 weight percent. The addition of germanium to the alloy may, under certain conditions, provide remarkable stability to the microstructure—in particular, to the ability of the alloy to maintain a very fine grain size even during the elevated temperatures used during superplastic processing.

**[0014]** Without being bound by theory, the germanium in the alloy may provide stability to the microstructure by pinning grain boundaries and thus inhibiting their growth. The pinning may be due to one or more mechanisms, such as by the formation of fine germanium-bearing precipitates, by a so-called "solute drag" mechanism (where dissolved species such as germanium serve to dissipate energy and thus inhibit grain boundary motion), or by a combination of such mechanisms. Certain methods of fabricating articles based on the alloy described herein, and which may take advantage of these stabilizing mechanisms, are explained in more detail later in this description. Other elements that may enhance the effects obtained with the germanium additions as set forth above

can be added to the alloy. The addition of one or more of these elements may allow for the control of precipitate size and morphology, such as, for example, the ability to control the lattice parameters of the precipitates to improve deformation characteristics of the alloy. Examples of such elements include silicon (up to about 2 weight percent), boron (up to about 1 weight percent), and phosphorous. In some embodiments the phosphorous is present from about 0.01 weight percent to about 2 weight percent. Combinations of these elements may also be used to good effect. For example, in some embodiments, the alloy comprises silicon and boron. In particular embodiments, the silicon is present at a level in the range from about 0.1 weight percent to about 1.5 weight percent and the boron is present at a level in the range from about 0.05 weight percent to about 0.4 weight percent. In other embodiments, the alloy comprises phosphorous and silicon. In particular embodiments, the phosphorous is present at a level in the range from about 0.01 weight percent to about 0.1 weight percent and the silicon is present at a level in the range from about 0.1 weight percent to about 1.5 weight percent.

**[0015]** The alloy described above is essentially free of martensite, meaning the alloy contains no more than about 5 volume percent of a martensite phase. The presence of martensite, generally an acicular phase, is detrimental to the plastic deformation characteristics desired for the articles described herein, as its sharp tips may induce stress concentrations that promote cracking during processing. In US Patent No. 6,921,441 to Tanaka et al., a titanium alloy is described, but the alloy in that reference is described to be "super-elastic," a property attributed to the presence of martensite formed during processing. In particular, the alloys described therein are stated to be "rapidly cooled," which is generally known in the art to be necessary to effect conversion to martensite. However, the alloys described herein are processed (for example, by controlling rates of cooling) to minimize the formation of martensite and thus preserve as much as possible the most advantageous microstructure for superplastic processing. Moreover, the alloy composition and processing are typically selected in combination to avoid martensite formation, resulting in microstructures typical of the so-called "near alpha" or "alpha-beta" titanium alloy classes referred to in the art.

**[0016]** In particular embodiments of the present invention, the alloy is made of about 6 weight percent aluminum, about 4 weight percent vanadium, and from about 0.05 weight percent to about 0.4 weight percent germanium. This alloy composition is expected to provide properties similar to the well-known "Ti-6-4" alloy, but with the added capability to stabilize a much finer grain size during superplastic processing at temperatures of interest than the conventional alloy can. Moreover, in some embodiments the alloy comprises from about 5.5 weight percent to about 6.5 weight percent aluminum; from about 1.8 weight percent to about 2.2 weight percent molybdenum; from about 3.6 weight percent to about 4.4 weight percent

zirconium; from about 1.8 weight percent to about 2.2 weight percent tin; and germanium in the range from about 0.05 weight percent to about 1 weight percent. This latter alloy is expected to provide similar properties to the well-known "Ti-6-2-4-2" alloy, but with the improved microstructural stability as described previously.

**[0017]** Methods in accordance with the present invention have been developed to take advantage of the excellent microstructural stability provided by the alloys described above. In one embodiment, a method for fabricating an article comprises providing a billet made of an alloy as described above, and stabilizing the billet microstructure (that is, the inherent structure of the alloy as it exists on the microscopic scale) to form a stabilized billet. The method, in some embodiments, further comprises superplastically processing the stabilized billet to form a processed item.

**[0018]** There are two alternatives for stabilizing the billet microstructure. A billet microstructure is said herein to be stabilized where certain microstructural constituents are disposed to retard the growth of grains during superplastic processing. Depending on the alloy composition, and the processing route followed, the microstructural constituents may be precipitates, solute atoms or clusters of solute atoms, or combinations including one or more of these.

**[0019]** The first alternative for stabilizing the billet microstructure is to heat the billet to a temperature and hold the billet at the temperature for a time sufficient to form a dispersion of precipitates in the billet. These precipitates are typically germanium-bearing, such as an intermetallic compound of germanium (that is, a germanide), but other precipitate types such as compounds containing silicon (for example, silicides), boron (for example, borides), phosphorous (for example, phosphides), or complex compounds of one or more of these elements, may be present. The actual composition of the precipitates will vary depending on the composition of the alloy. In certain embodiments the precipitates comprise a germanide, such as titanium germanide ( $\text{Ti}_5\text{Ge}_3$ ). One skilled in the art will appreciate that the temperature selected is generally below a solvus temperature of the precipitate in the alloy, and the solvus temperature can be readily deduced when the composition of the precipitate is known, or measured using commonly known calorimetric analysis techniques, for example. In some embodiments this solvus temperature is in the range from about 400°C to about 1000°C. In some embodiments the temperature to which the billet is heated to form the precipitate dispersion is some specified offset from the solvus temperature, for instance about 100 degrees below the solvus temperature. The time for which the billet is held at a given temperature is selected to provide a dispersion having a desirable volume fraction and size distribution. Fine precipitates (i.e., much smaller than the grain size of the billet) are generally desired to ensure a high degree of efficacy in retarding grain growth. In some embodiments, the dispersion in the stabilized billet has

a median precipitate size up to about the grain size of the alpha phase in the alloy (see below). The time selected is a function of temperature, in that a relatively high temperature treatment requires a comparatively lower time to form the desired dispersion when compared to a lower temperature treatment, according to physical metallurgy principles well understood in the art. It should be noted that although precipitates are formed and may be applied to retard grain growth in the billet, other mechanisms, such as solute drag, may also be operative, especially where there is an excess of germanium and other solute elements present in the alloy even after the precipitation treatment is stopped.

**[0020]** Another alternative for stabilizing the billet microstructure is to heat the billet to a temperature above the precipitate solvus temperature and thus allow at least some dissolution of the precipitates to occur. In some embodiments, the time that the alloy is held at temperature is sufficient to dissolve substantially all of one or more type of precipitates in the alloy, such as germanium-bearing precipitates. This alternative emphasizes the solute drag mechanism of grain growth inhibition, but, because some precipitates (germanium-bearing or otherwise) may, in some instances, still be left undissolved, the precipitate pinning mechanism may also be operative in this embodiment as well. In some embodiments, the temperature selected for the dissolution treatment is in the range from about 50°C to about 100°C above the solvus temperature of the precipitate(s) of interest.

**[0021]** The billet may be provided by providing a starting material, which is then thermomechanically processed to provide a billet for later processing by superplastic processing. The starting material may be provided using any of the well understood metallurgical processes commonly used in the metalworking industry. For example, one processing route to providing the starting material includes casting an ingot, and then giving the ingot a thermomechanical "upset" treatment to break up its as-cast structure and to promote a more homogeneous distribution of compositional constituents throughout the microstructure. Alternatively, the starting material may be fabricated using powder metallurgy processes. Starting material may have precipitates present, or may be provided or treated to be free of precipitates.

**[0022]** The starting material, in some embodiments, is given a thermomechanical treatment to form a billet having desired characteristics (such as grain size distribution) to allow efficient superplastic processing. As used herein, the grain size of the alloy is defined by the grain size of the alpha phase; beta phase may be present with a different size distribution than the alpha phase. In some embodiments, the billet has a median grain size of less than about 2 micrometers. In certain embodiments, the median grain size is even finer, such as less than about 1 micrometer or, in some embodiments, as fine as less than about 500 nanometers. Finer grain size for the billet generally allows superplastic processing to occur at lower temperatures, which, as related above, results in a

lower cost process overall.

**[0023]** The thermomechanical processing of the starting material into the billet, in some embodiments, includes processing via one or more so-called "Severe Plastic Deformation" (SPD) methods. As used herein, SPD is defined as a process by which large strains, typically greater than 1, are imparted to a material without significantly changing the starting cross section of the material. SPD is particularly attractive in certain embodiments due to its ability to produce very fine grained material, even in large parts, via the introduction of large amounts of strain energy into the workpiece. Various SPD processes are known in the art, including Multi-Axis Forging, Twist Extrusion, and Equal-Channel Angular Extrusion; each is suitable for use as the SPD step described herein. For instance, in one embodiment, the SPD process includes Multi-Axis Forging. In this process, a workpiece undergoes a conventional forging operation under carefully controlled temperatures and strain rates. Between each forging pass, the workpiece is re-oriented such that each subsequent forging step is carried out in a direction orthogonal to the previous two passes. By reorienting the workpiece, strains on the order of approximately 1 to 6 may be accumulated without reducing the cross section of the workpiece.

**[0024]** Once the stabilized billet with fine grain size is produced, it is then, in some embodiments, superplastically processed, thereby converting the billet into a processed item. Alternatively, the process may be ended with the stabilizing step, and the article thus comprises a feedstock to be used in some future fabrication process.

**[0025]** Superplastic processing generally occurs in a processing regime of strain rate and temperature suitable to allow the very large strains characteristic of this process; the term superplastic processing is generally accepted to mean a process that occurs in a regime where the material's strain rate sensitivity coefficient is greater than 0.3. The selection of strain rate and temperature may be based in part on the composition and grain size of the workpiece; one skilled in the art can readily make this selection given the information about composition, grain size, and desired total strain. Because the alloy described above may be stabilized with an ultra-fine grain size, it may be superplastically processed at temperatures below those typically used in the industry for conventional materials. For instance, conventional titanium alloys are generally superplastically processed at temperatures above half of an alloy's homologous temperature; the attributes described above may allow for successful superplastic processing at temperatures below this.

## EXAMPLES

**[0026]** Without further elaboration, it is believed that one skilled in the art can, using the description herein, utilize the present invention to its fullest extent. The following examples are included to provide additional guid-

ance to those skilled in the art in practicing the claimed invention. The examples provided are merely representative of the work that contributes to the teaching of the present application. Accordingly, these examples are not intended to limit the invention, as defined in the appended claims, in any manner.

**[0027]** To promote the thermal stability of a fine-grained titanium alloy capable of superplastic processing, alloying additions were considered. One criterion for alloying element selection was based upon the ability to provide a solute drag effect for grain boundaries or to form stable precipitates that may pin grain boundaries, maintaining superplasticity at processing temperatures. Further criteria for alloying element selection were designed to meet processing requirements and minimize the effect on other alloy properties. Generally, these criteria involved thermodynamic properties of precipitates expected to form when the particular elements were added to the alloy, and the effects of these elements on phase transformation behavior of the resultant alloy.

**[0028]** Alloying elements that met these criteria and provided a range of valence states, atomic weights and sizes, and solubility limits were B, Si, P, and Ge. The intermetallics present in the binary phase diagrams were TiB, Ti<sub>3</sub>Si, Ti<sub>3</sub>P, and Ti<sub>5</sub>Ge<sub>3</sub>.

**[0029]** Eighteen compositions designed to test the precipitate forming and segregation characteristics of alloying element combinations were vacuum arc-melted. They were examined in both the as-melted and heat-treated conditions, where the homogenizing and precipitate-forming heat treatment consisted of 96 minutes at 1200°C followed by furnace cooling at a rate of 1°C per minute. Precipitates were identified using X-ray diffraction (XRD) and Scanning Electron Microscopy-based analyses including microprobe (WDS), Energy Dispersive Spectroscopy (EDS), and Electron Backscatter Diffraction (EBSD).

**[0030]** Notable results included the solubility of Si in certain germanides, P and Ge in silicides, and Si and Ge in borides. In some cases, a shift in the lattice parameters of a particular phase was detectable by XRD depending on the composition. The phase Ti<sub>6</sub>(Ge,Si)<sub>2</sub>B (described, for instance in A. S. Ramos et al., *Intermetallics* 12 (2004), 487-91; and D. B. Borisov et al., *Powder Metallurgy and Metal Ceramics* 46 (2007), 153-162) was found to exist in alloys with additional elements beyond the phase components for the first time. Additionally, the addition of Ge in certain alloying compositions promoted a fine dispersion of the Ti<sub>5</sub>Ge<sub>3</sub> type phase and Ge in solution upon casting, with subsequent growth of the precipitate upon heat treatment.

**[0031]** While only certain features of the invention have been illustrated and described herein, many modifications and changes will occur to those skilled in the art. It is, therefore, to be understood that the appended claims are intended to cover all such modifications and changes as fall within the true spirit of the invention.

**[0032]** For completeness, various aspects of the in-

vention are now set out in the following numbered clauses:

1. An article comprising:
  - an alloy substantially free of martensite, wherein the alloy comprises at least about 75 weight percent titanium;
  - up to about 10 weight percent of a beta stabilizing component;
  - from about 3 weight percent to about 15 weight percent of an alpha stabilizing component; and
  - from about 0.05 weight percent to about 5 weight percent germanium.
2. The article of clause 1, wherein the alloy further comprises up to about 2 weight percent silicon.
3. The article of clause 1, wherein the alloy further comprises up to about 1 weight percent boron.
4. The article of clause 1, wherein the alloy further comprises silicon and boron.
5. The article of clause 4, wherein the silicon is present at a level in the range from about 0.1 weight percent to about 1.5 weight percent and the boron is present at a level in the range from about 0.05 weight percent to about 0.4 weight percent.
6. The article of clause 1, wherein the alloy further comprises phosphorous.
7. The article of clause 6, wherein the phosphorous is present at a level of in the range from about 0.01 weight percent to about 2 weight percent.
8. The article of clause 1, wherein the alloy further comprises phosphorous and silicon.
9. The article of clause 8, wherein the phosphorous is present at a level in the range from about 0.01 weight percent to about 0.1 weight percent and the silicon is present at a level in the range from about 0.1 weight percent to about 1.5 weight percent.
10. The article of clause 1, wherein the beta stabilizing component is present at a level in the range from about 3.5 weight percent to about 4.5 weight percent.
11. The article of clause 1, wherein the beta stabilizing component comprises at least one material selected from the group consisting of refractory metals, platinum group metals, and transition metals.

12. The article of clause 1, wherein the beta stabilizing component comprises at least one material selected from the group consisting of molybdenum, vanadium, tantalum, niobium, manganese, iron, chromium, cobalt, nickel, rhenium, palladium, tungsten, zirconium, and copper.

13. The article of clause 1, wherein the beta stabilizing component comprises at least one material selected from the group consisting of vanadium, molybdenum, niobium, tantalum, and iron.

14. The article of clause 1, wherein the alpha stabilizing component is present at a level in the range from about 5.5 weight percent to about 6.75 weight percent.

15. The article of clause 1, wherein the alpha stabilizing component comprises at least one material selected from the group consisting of tin, aluminum, gallium, lanthanum, cerium, carbon, oxygen, and nitrogen.

16. The article of clause 1, wherein the alpha stabilizing component comprises at least one material selected from the group consisting of aluminum and tin.

17. The article of clause 1, wherein the alloy comprises  
about 6 weight percent aluminum;  
about 4 weight percent vanadium; and  
from about 0.05 weight percent to about 0.4 weight percent germanium.

18. The article of clause 1, wherein the alloy comprises  
from about 5.5 weight percent to about 6.5 weight percent aluminum;  
from about 1.8 weight percent to about 2.2 weight percent molybdenum;  
from about 3.6 weight percent to about 4.4 weight percent zirconium;  
from about 1.8 weight percent to about 2.2 weight percent tin;  
wherein the germanium content is in the range from about 0.05 weight percent to about 1 weight percent.

19. The article of clause 1, wherein the article comprises a component of a turbine assembly.

20. The article of clause 19, wherein the component is an engine mount, a liner, a heat shield, a gear-box casing, a bladed disk, or a blade.

21. The article of clause 1, wherein the article is a feedstock suitable for a fabrication process.

22. A method for forming an article, the method com-

prising:

providing a billet comprising an alloy substantially free of martensite, wherein the alloy comprises

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at least about 75 weight percent titanium,

up to about 10 weight percent of a beta stabilizing component,

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from about 3 weight percent to about 15 weight percent of an alpha stabilizing component, and

from about 0.05 weight percent to about 5 weight percent germanium; and

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stabilizing the billet microstructure, thereby forming a stabilized billet.

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23. The method of clause 22, further comprising superplastically processing the stabilized billet to form a processed item.

24. The method of clause 22, wherein stabilizing the billet microstructure comprises heating the billet to a temperature and holding the billet at the temperature for a time sufficient to form a dispersion of precipitates in the billet.

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25. The method of clause 24, wherein the precipitates comprise an intermetallic compound of germanium.

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26. The method of clause 25, wherein the precipitates comprise titanium germanide.

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27. The method of clause 24, wherein the dispersion has a median precipitate size up to a grain size of the alloy.

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28. The method of clause 24, further comprising dissolving the precipitates after the superplastic processing step and heat treating the processed item.

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29. The method of clause 22, wherein stabilizing the billet microstructure comprises heating the billet to a temperature and holding the billet at the temperature for a time sufficient to dissolve at least some germanium-bearing precipitates.

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30. The method of clause 22, wherein providing the billet comprises providing a starting material and thermomechanically processing the starting material.

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31. The method of clause 30, wherein thermome-

chanically processing comprises processing via a Severe Plastic Deformation process.

32. The method of clause 31, wherein the Severe Plastic Deformation process comprises Multi-Axis Forging.

33. The method of clause 22, wherein the billet comprises a plurality of grains having a median grain size less than about 2 micrometers.

34. The method of clause 22, wherein the billet comprises a plurality of grains having a median grain size less than about 1 micrometer.

35. The method of clause 22, wherein the billet comprises a plurality of grains having a median grain size less than about 500 nanometers.

36. The method of clause 23, further comprising heat treating the processed item to attain a desired grain size in the processed item.

## Claims

### 1. An article comprising:

an alloy substantially free of martensite, wherein the alloy comprises at least about 75 weight percent titanium;  
up to about 10 weight percent of a beta stabilizing component;  
from about 3 weight percent to about 15 weight percent of an alpha stabilizing component; and  
from about 0.05 weight percent to about 5 weight percent germanium.

2. The article of claim 1, wherein the alloy further comprises up to about 2 weight percent silicon.

3. The article of claim 1 or claim 2, wherein the alloy further comprises up to about 1 weight percent boron.

4. The article of any preceding claim, wherein the alloy further comprises phosphorous.

5. The article of claim 4, wherein the phosphorous is present at a level of in the range from about 0.01 weight percent to about 2 weight percent.

6. The article of any preceding claim, wherein the beta stabilizing component comprises at least one material selected from the group consisting of refractory metals, platinum group metals, and transition metals.

7. The article of any preceding claim, wherein the beta stabilizing component comprises at least one material selected from the group consisting of molybdenum, vanadium, tantalum, niobium, manganese, iron, chromium, cobalt, nickel, rhenium, palladium, tungsten, zirconium, and copper. 5
8. The article of any preceding claim, wherein the alpha stabilizing component comprises at least one material selected from the group consisting of tin, aluminum, gallium, lanthanum, cerium, carbon, oxygen, and nitrogen. 10
9. The article of any preceding claim, wherein the alloy comprises at least about 75 weight percent titanium, about 6 weight percent aluminum; about 4 weight percent vanadium; and from about 0.05 weight percent to about 0.4 weight percent germanium. 15  
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10. The article of any one of claims 1 to 8, wherein the alloy comprises at least about 75 weight percent titanium, from about 5.5 weight percent to about 6.5 weight percent aluminum; 25  
from about 1.8 weight percent to about 2.2 weight percent molybdenum; from about 3.6 weight percent to about 4.4 weight percent zirconium; 30  
from about 1.8 weight percent to about 2.2 weight percent tin; wherein the germanium content is in the range from about 0.05 weight percent to about 1 weight percent.
11. A method for forming an article, the method comprising: 35  
  - providing a billet comprising an alloy substantially free of martensite, wherein the alloy comprises 40  
at least about 75 weight percent titanium, up to about 10 weight percent of a beta stabilizing component, from about 3 weight percent to about 15 weight percent of an alpha stabilizing component, and 45  
from about 0.05 weight percent to about 5 weight percent germanium; and stabilizing the billet microstructure, thereby forming a stabilized billet. 50
12. The method of claim 11, further comprising superplastically processing the stabilized billet to form a processed item.
13. The method of claim 11 or claim 12, wherein stabilizing the billet microstructure comprises heating the billet to a temperature and holding the billet at the temperature for a time sufficient to form a dispersion 55  
of precipitates in the billet.
14. The method of claim 13, wherein the precipitates comprise an intermetallic compound of germanium.
15. The method of claim 13 or claim 14, further comprising dissolving the precipitates after the superplastic processing step and heat treating the processed item.





## EUROPEAN SEARCH REPORT

Application Number  
EP 10 16 1351

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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Place of search Munich		Date of completion of the search 17 June 2010	Examiner Brown, Andrew
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
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