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(54) **HIGH-PURITY TITANIUM-NICKEL ALLOYS
WITH SHAPE MEMORY**

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(57) **ABSTRACT**

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The invention includes an alloy containing equivalent amounts of nickel and titanium. The alloy has shape memory and a metallic purity of at least about 99.995%, and comprises less than about 200 ppm of gases. The invention also includes an alloy comprising titanium and nickel where the titanium and nickel amounts are non-equivalent. The alloy has shape memory and has a metallic purity of at least 99.995%, and contains less than about 200 ppm of gases. The invention further includes a method of producing a shape memory alloy. Titanium is provided having a metallic purity of at least 99.999% and nickel is provided having a metallic purity of at least 99.99%. The titanium and nickel are combined utilizing at least one melting event independently selected from e-beam melting, vacuum arc melting, vacuum induction melting, induction skull melting and plasma melting.

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HIGH-PURITY TITANIUM-NICKEL ALLOYS WITH SHAPE MEMORY

RELATED PATENT DATA

[0001] This patent claims benefit of priority under 35 U.S.C. §119 to U.S. Provisional Patent Ser. No. 60/514,317, which was filed Oct. 24, 2003.

TECHNICAL FIELD

[0002] The invention pertains to shape memory alloys and methods of producing shape memory alloys.

BACKGROUND OF THE INVENTION

[0003] Shape memory materials are materials which can recover a shape after heating. The shape memory properties of shape memory alloys such as, for example, nickel-titanium based shape memory alloys, can overlap with super-elastic properties. Super-elastic properties which exist over a temperature range specific to the particular material allow shape memory materials to have great flexibility. The unique properties of shape memory alloys make them particularly useful for applications in fields such as automotive, aerospace, thin-film, robotics, and medical fields. Exemplary applications for these materials include implantable medical devices, precision tools and medical instruments, and actuators. Nickel-titanium based alloys are currently being used in place of stainless steel in many applications. Other exemplary applications for these materials include sputtering targets which in turn can be utilized to produce thin films such as those used in the manufacture of micro-electromechanical systems (MEMS).

[0004] Shape memory, super-elasticity and other metallurgical properties of a material can be affected by contaminants in the material. For example, contaminants such as metallic impurities and/or gases can impair mechanical properties by forming inclusions that can lower fatigue life and can shift phase transformation temperatures out of specification. The presence of such contaminants can also influence the effects of additional alloying elements, and can cause unpredictability, variability and inconsistency in mechanical and transformation properties of the resulting alloys. Even in binary alloys such as binary nickel-titanium alloys, the presence of contaminants can vary the mechanical properties, corrosion resistance, and/or phase transformation properties of the material.

[0005] Nickel-titanium alloys having limited purities attainable utilizing conventional methodologies typically have high work hardening rates which limit the cross-sectional reduction during many fabrication operations. These conventional materials require numerous in-process heat treatments to regain ductility. Further, the presence of contaminants can affect the biocompatibility of materials. Accordingly, it is desirable to develop methods to produce high-purity shape memory alloys.

SUMMARY OF THE INVENTION

[0006] In one aspect the invention encompasses an alloy containing atomically equivalent amounts of nickel and titanium. The alloy has a shape memory and has a metallic purity of at least about 99.995%, by weight, and comprises less than about 200 ppm of gases.

[0007] In one aspect the invention encompasses an alloy comprising titanium and nickel where the titanium and nickel amounts are non-equivalent. The alloy has shape memory and has a metallic purity of at least 99.995%, by weight, and contains less than about 200 ppm of gases.

[0008] In one aspect the invention encompasses a method of producing a shape memory alloy. Titanium is provided which has a metallic purity of at least 99.999%, by weight. Nickel is provided which has a metallic purity of at least 99.99%, by weight, and the titanium and nickel are combined to form the alloy. The combining utilizes a first melting event and a second melting event where each of the first and second melting events can be e-beam melting, vacuum arc melting, vacuum induction melting, induction skull melting or plasma melting.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0009] This disclosure of the invention is submitted in furtherance of the constitutional purposes of the U.S. Patent Laws "to promote the progress of science and useful arts" (Article 1, Section 8).

[0010] The invention encompasses high-purity titanium alloys and methodology for producing high-purity titanium alloys. The methodology of the invention can be utilized for producing shape-memory and/or super-elastic titanium alloy materials. The high-purity alloy materials of the invention have improved cold-ductility allowing fewer in-process heat treatments relative to conventional materials.

[0011] The term 'shape memory' as used in the description of the invention, refers to materials which recover an original shape after heating to above a temperature at which the material begins to undergo a solid state phase change from martensite to austenite. The temperature at which this transformation begins can be referred to as the phase transformation temperature or critical temperature, and can be dependent upon the particular alloy or material. When a shape memory material is cooled to below the critical temperature it exists in the martensite phase and is malleable and deformable. Upon heating through the critical temperature, a shape memory material that has been deformed in the martensite phase will regain the austenite phase and substantially resume a shape that it held prior to the cooling and deformation.

[0012] In particular instances, super-elastic properties present in shape memory materials can allow a martensite phase to be induced by placing stress upon the material without subjecting the material to a temperature below the critical temperature. The material can then be deformed in the martensite phase. Relief from the stress upon the material can induce return to the austenite phase and recovery of the earlier shape that existed prior to the stress/deformation process.

[0013] Methodology of the invention can be useful for production of numerous titanium alloys and can be particularly useful for production of high-purity nickel-titanium based (nitinol) binary and higher order alloys. For purposes of the description, the term high-purity can refer to a metallic purity of greater than 99.995% (4N5), where such material contains a total metallic impurity content of less than or equal to about 50 ppm, by weight. In particular

instances, high-purity materials of the invention will have a purity of greater than or equal to 99.998% (4N8), by weight, such material containing less than or equal to 20 ppm total metallic impurities. The methodology of the invention can be utilized to produce binary, ternary or higher order Ni—Ti based high-purity materials.

[0014] In particular instances, the high-purity Ni—Ti alloy produced by methodology of the invention can have a 1:1 atomic ratio of nickel and titanium. Accordingly, a binary Ni—Ti alloy will contain an atomic equivalent of nickel and titanium which can be alternatively referred to as a 50% nickel binary alloy. Ternary and higher order alloys can also be produced having an atomic equivalence of nickel and titanium. For these higher order alloys, the total atomic percent of nickel and titanium can depend upon the amount of additional elements added to the alloy.

[0015] In addition to the alloys having an atomic equivalent of nickel and titanium described above, the invention additionally encompasses alloys having an atomic excess of nickel relative to titanium, or an atomic excess of titanium over the amount of nickel present. For example, excess nickel of up to about 1 at % can be utilized to adjust the transformation temperature of a material and/or to increase the yield strength. The excess of either Ni or Ti is not limited to a particular value. In non-binary Ni—Ti based alloys according to the invention, additional elements can be added to affect various properties. For example, one or more non-Ti/Ni metallic elements can be added to increase or decrease the transformation temperature of the material, affect the deformation stress, and/or decrease the hysteresis of the material. The addition of one or more non-Ni/Ti elements can be utilized in higher order alloys having an atomic equivalence of nickel and titanium or alloys having an atomic excess of either nickel or titanium.

[0016] For production of higher order alloys according to the invention, one or more metallic elements can be utilized. The amount of added element(s) is not limited to a particular value. Nor is the addition limited to any particular element or combination of elements. In particular instances the added element(s) can comprise one or more metallic element such as Nb, Hf, Ta, Pt, Pd, Au, Zr, Fe, V, Mo, W, Ru, Cr, Cu, and combinations thereof.

[0017] High-purity alloys of the invention can be produced to contain from 0 to less than about 200 ppm of gases. As utilized in the present description, ppm refers to parts per million by weight. The term “gases” as utilized in the present description can refer to contaminant elements which are generally considered to be interstitial elements, including O, C, S, N, and H. In particular instances, the alloys of the present invention can preferably contain from 0 to less than 100 ppm of total gases, and more preferably less than about 50 ppm. In particular, the C content can preferably be less than 50 ppm and more preferably less than 20 ppm. The S content can be preferably less than 5 ppm and more preferably less than 2 ppm. The H content can be preferably less than 5 ppm and more preferably less than 2 ppm. The indicated preferred values for gas contaminants are values as measured by the LECO technique. In particular aspects, alloys of the present invention can contain 0 ppm of one or more of these gases or can contain one or more gases below the corresponding detection limit of the technique. For purposes of the description, where an element may be

present in a material at an amount below detection limit for the element, the material can be referred to as being substantially free of the element.

[0018] As indicated above, alloys of the present invention can preferably contain less than or equal to 50 ppm of total metallic impurities, where metallic impurities refers to any metallic element present which is not intentionally added. In particular aspects, it can be preferable that the alloys of the present invention contain no more than 50 ppm Fe, and preferably from 0 to less than 10 ppm Fe. Any chromium present can preferably be less than 5 ppm and more preferably less than 1 ppm. Any cobalt present can preferably be less than 1 ppm and more preferably less than 0.5 ppm. Any tungsten present can preferably be less than 10 ppm, and more preferably from 0 to less than 5 ppm. A total of all other metallic impurities present in the alloys of the invention can preferably be from 0 to less than 5 ppm each. The indicated content of metallic impurities within alloys of the invention reflects values as measured utilizing glow discharge mass spectrometry (GDMS).

[0019] It is to be understood that in particular instances, alloys of the invention can contain 0 ppm of any given metallic impurity or can contain one or more metallic impurity at levels below corresponding detection limits of the technique. For purposes of the description, where a metallic element may be present in a material at an amount below detection limit for the element, the material can be referred to as being substantially free of the element.

[0020] Methodology of the invention for producing the described titanium alloys includes utilizing high-purity titanium during the alloying process. Such high-purity titanium can preferably be titanium having a purity of at least 99.999% with ultra low dissolved gases and carbon levels. Such ultra pure titanium can be produced utilizing methodology and apparatus described in U.S. Pat. Nos. 6,063,254 and 6,024,847, the contents of which are hereby incorporated by reference.

[0021] For titanium-nickel based alloys of the invention, the described high-purity titanium can be combined with a high-purity source of nickel. In particular instances, the high-purity nickel source can preferably have a purity of at least 99.99%.

[0022] For ternary and higher order alloys in accordance with the invention, non-titanium/nickel alloying elements are preferably provided utilizing a high-purity source, and most preferably from a source having a purity level of sufficient to enable an alloy purity of at least 99.995%, preferably 99.998%, by weight.

[0023] Production of titanium-nickel based high-purity alloys of the invention can comprise combination of high-purity titanium with high-purity nickel, and optionally with one or more high-purity sources of additional elements. Although the combining can, in particular instances, utilize a single melting event, the combining preferably comprises at least two melting events. Such melting events can include, for example, e-beam melting, vacuum arc remelting, vacuum induction melting, induction skull melting, plasma melting, or combinations thereof.

[0024] The invention contemplates alloy production utilizing multiple applications of a single melting technology or utilization of more than one melting technology. It can be

advantageous to utilize multiple melting events to provide improved purity and homogeneity of the resulting material. Including at least one high vacuum melting event can beneficially preserve the purity of the source materials by avoiding imparting impurities during processing. Accordingly, alloys of the invention can have a purity equivalent to that of the starting materials.

[0025] Particular applications of the invention can advantageously include at least one e-beam melting operation and at least one additional melting event for production of high-purity nickel-titanium based alloys. The use of e-beam melting can, in some instances further increase the purity by removing at least some of the impurities present in the source materials. Accordingly, in some instances alloys prepared in accordance with the invention can have an increased purity relative to the starting materials.

EXAMPLE

Production of a High-Purity Ni—Ti Alloy

[0026] Titanium having a 99.9997% purity and nickel having a purity of 99.997% were combined and were vacuum arc re-melted to form a Ni—Ti binary alloy containing approximately 55.8 wt % Ni. The resulting alloy had a purity of 99.997%, by weight. Purity analysis of the Ni—Ti binary alloy presented in Tables 1 and 2.

TABLE 1

Ni—Ti Binary Alloy (approximately 55.8 wt % Ni); Analysis of Metallic Impurities	
Metallic Impurities*	Concentration [ppm wt]
Al	0.69
B	0.01
Co	0.79
Cr	0.93
Cu	3.40
Fe	5.90
Hf	0.02
Mg	0.02
Mn	0.06
P	0.01
Re	0.01
Si	0.23
V	0.25
W	8.40
Zr	1.00
Others	< detection limit
Total metallic impurities	21.72

*Measurement technique GDMS

[0027]

TABLE 2

Ni—Ti Binary Alloy (approximately 55.8 wt % Ni); Analysis of Gas Contaminants	
LECO Analysis	Concentration [ppm wt]
O	99
C	33
N	1
S	<1
H	2

[0028] Processing in accordance with the invention can additionally include various thermo-mechanical processing steps, including but not limited to, forging, rolling, drawing, and annealing. The described thermo-mechanical processing of the high-purity alloys can be utilized to produce materials having desired shape memory and super-elastic properties with purity levels that exceed levels attainable utilizing conventional alloy formation and processing methods.

[0029] As indicated above, alloy production in accordance with the methodology of the invention can be particularly useful for minimizing or eliminating incorporation of any contaminants into high-purity materials during alloy formation. Due to the use of high-purity source metals in combination with melting techniques that can maintain or increase purity, alloys produced by methodology of the present invention can have a level purity equal to or exceeding the original high-purity source materials.

[0030] In compliance with the statute, the invention has been described in language more or less specific as to structural and methodical features. It is to be understood, however, that the invention is not limited to the specific features shown and described, since the means herein disclosed comprise preferred forms of putting the invention into effect. The invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims appropriately interpreted in accordance with the doctrine of equivalents.

1. An alloy comprising:

a nickel content; and

a titanium content atomically equivalent to the nickel content, the alloy having shape memory and having a metallic purity of at least about 99.995%, by weight and comprising less than about 200 ppm of gases, by weight.

2. The alloy of claim 1 wherein the alloy is a binary alloy.

3. The alloy of claim 1 wherein the alloy further comprises at least one additional metal.

4. The alloy of claim 3 wherein the at least one additional metal is selected from the group consisting of Nb, H, Ta, Pt, Pd, Au, Zr, Fe, V, Mo, W, Ru, Cr, and Cu.

5. (canceled)

6. The alloy of claim 3 wherein a total amount of the at least one additional metal present in the alloy is exceeded by a combined amount of Ni and Ti.

7. The alloy of claim 1 wherein the metallic purity of the alloy is at least 99.998%, by weight.

8. The alloy of claim 1 comprising less than or equal to 1 ppm each (by weight) of metallic impurities selected from the group consisting of Al, Co, and Zr.

9. The alloy of claim 1 comprising less than or equal to 50 ppm Fe, by weight.

10. The alloy of claim 1 comprising less than or equal to 10 ppm W, by weight.

11. The alloy of claim 1 comprising less than or equal to 5 ppm Cr, by weight.

12. The alloy of claim 1 comprising less than or equal to 0.25 ppm each (by weight) of metallic impurities selected from the group consisting of V, Si, B, Hf, Mg, Mn, P, and Re.

13. The alloy of claim 1 comprising less than or equal to 0.1 ppm each (by weight) of metallic impurities selected from the group consisting of B, Hf, Mg, Mn, P, and Re.

14. The alloy of claim 1 comprising less than or equal to 100 ppm O, by weight.

15. The alloy of claim 1 comprising less than or equal to 50 ppm C, by weight.

16. The alloy of claim 1 comprising less than or equal to 3 ppm N, by weight.

17. The alloy of claim 1 comprising less than or equal to 5 ppm S, by weight.

18. The alloy of claim 1 comprising less than or equal to 5 ppm H, by weight.

19. An alloy comprising:

titanium; and

nickel, an atomic amount of nickel present in the alloy exceeding the atomic amount of titanium present in the alloy, the alloy having shape memory and having a metallic purity of at least about 99.995%, by weight and comprising less than about 200 ppm of gases, by weight.

20. The alloy of claim 19 wherein the amount of nickel exceeds the amount of titanium by from greater than 0 at % to about 1 at %.

21. The alloy of claim 19 wherein the alloy is a binary alloy.

22. The alloy of claim 19 wherein the alloy further comprises at least one additional metal.

23. The alloy of claim 22 wherein the at least one additional metal is selected from the group consisting of Nb, Hf, Ta, Pt, Pd, Au, Zr, Fe, V, Mo, W, Ru, Cr, and Cu.

24. (canceled)

25. The alloy of claim 22 wherein a total amount of the at least one additional metal present in the alloy is exceeded by a combined amount of Ni and Ti.

26. The alloy of claim 19 wherein the metallic purity of the alloy is at least 99.998%, by weight.

27. The alloy of claim 19 comprising less than or equal to 1 ppm each (by weight) of metallic impurities selected from the group consisting of Al, Co, and Zr.

28. The alloy of claim 19 comprising less than or equal to 50 ppm Fe, by weight.

29. The alloy of claim 19 comprising less than or equal to 10 ppm W, by weight.

30. The alloy of claim 19 comprising less than or equal to 5 ppm Cr, by weight.

31. The alloy of claim 19 comprising less than or equal to 0.25 ppm (by weight) each of metallic impurities selected from the group consisting of V, Si, B, Hf, Mg, Mn, P, and Re.

32. The alloy of claim 19 comprising less than or equal to 0.1 ppm (by weight) each of metallic impurities selected from the group consisting of B, Hf, Mg, Mn, P, and Re.

33. The alloy of claim 19 comprising less than or equal to 100 ppm O, by weight.

34. The alloy of claim 19 comprising less than or equal to 50 ppm C, by weight.

35. The alloy of claim 19 comprising less than or equal to 3 ppm N, by weight.

36. The alloy of claim 19 comprising less than or equal to 5 ppm S, by weight.

37. The alloy of claim 19 comprising less than or equal to 5 ppm H, by weight.

38. An alloy comprising:

nickel; and

titanium, an atomic amount of titanium present in the alloy exceeding the atomic amount of nickel present in the alloy, the alloy having shape memory and having a metallic purity of at least about 99.995%, by weight and comprising less than about 200 ppm of gases, by weight.

39. The alloy of claim 38 wherein the amount of titanium exceeds the amount of nickel by from greater than 0 at % to about 1 at %.

40. The alloy of claim 38 wherein the alloy is a binary alloy.

41. The alloy of claim 38 wherein the alloy further comprises at least one additional metal.

42. The alloy of claim 41 wherein the at least one additional metal is selected from the group consisting of Nb, Hf, Ta, Pt, Pd, Au, Zr, Fe, V, Mo, W, Ru, Cr, and Cu.

43. (canceled)

44. The alloy of claim 41 wherein a total amount of the at least one additional metal present in the alloy is exceeded by a combined amount of Ni and Ti.

45. The alloy of claim 38 wherein the metallic purity of the alloy is at least 99.998%, by weight.

46. The alloy of claim 38 comprising less than or equal to 1 ppm each (by weight) of metallic impurities selected from the group consisting of Al, Co, and Zr.

47. The alloy of claim 38 comprising less than or equal to 50 ppm Fe, by weight.

48. The alloy of claim 38 comprising less than or equal to 10 ppm W, by weight.

49. The alloy of claim 38 comprising less than or equal to 5 ppm Cr, by weight.

50. The alloy of claim 38 comprising less than or equal to 0.25 ppm (by weight) each of metallic impurities selected from the group consisting of V, Si, B, Hf, Mg, Mn, P, and Re.

51. The alloy of claim 38 comprising less than or equal to 0.1 ppm (by weight) each of metallic impurities selected from the group consisting of B, Hf, Mg, Mn, P, and Re.

52. The alloy of claim 38 comprising less than or equal to 100 ppm O, by weight.

53. The alloy of claim 38 comprising less than or equal to 50 ppm C, by weight.

54. The alloy of claim 38 comprising less than or equal to 3 ppm N, by weight.

55. The alloy of claim 38 comprising less than or equal to 5 ppm S, by weight.

56. The alloy of claim 38 comprising less than or equal to 5 ppm H, by weight.

57-65. (canceled)

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