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(54) NICKEL-TITANIUM ALLOY WITH A NON-ALLOYED DISPERSION AND METHODS OF MAKING SAME

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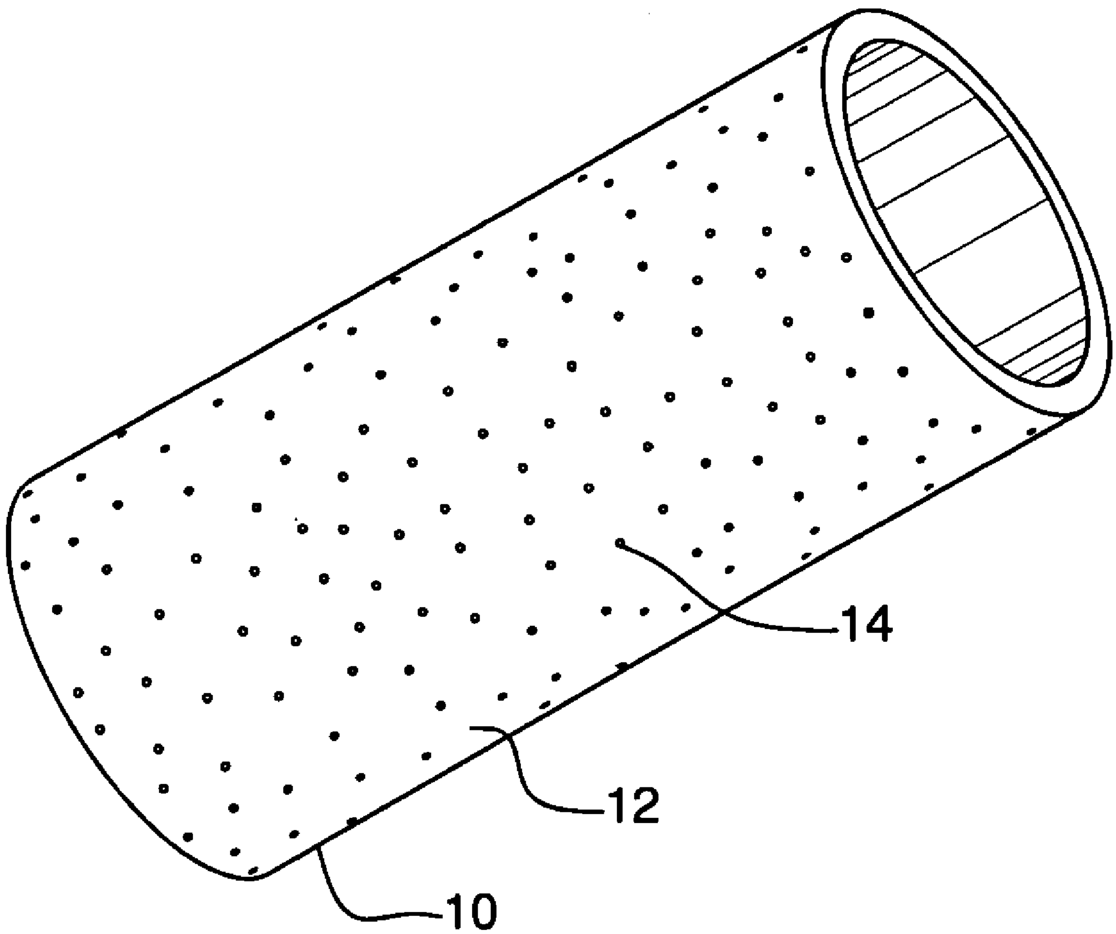
(57) **ABSTRACT**

An article having a nickel-titanium alloy and a homogeneous dispersion of discrete particles. The discrete particles are substantially free of nickel and titanium. A method of making the article includes melting a substantially equiatomic composition of nickel and titanium to form an alloy and dispersing a discrete particle in the alloy to form an ingot. The melting and dispersing are performed at a temperature above the alloying temperature of the composition and below the melting temperature of the discrete particle. The ingot is hot worked to form a processed ingot. The processed ingot is cold worked and annealed to form the article.



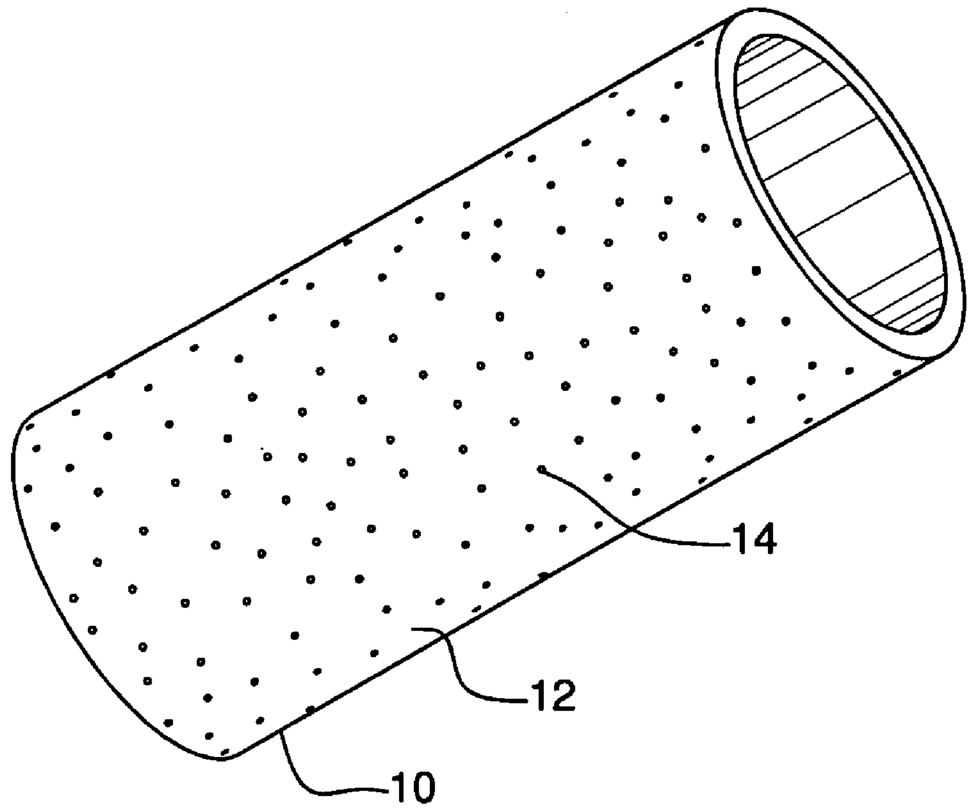


FIG. 1

NICKEL-TITANIUM ALLOY WITH A NON-ALLOYED DISPERSION AND METHODS OF MAKING SAME

FIELD OF THE INVENTION

[0001] The material and methods disclosed herein relate to a nickel-titanium alloy, and a nickel-titanium alloy with a dispersion of discrete particles substantially free of nickel and titanium.

BACKGROUND OF INVENTION

[0002] Nickel-titanium alloy, more specifically nitinol, is valued in a number of industries because of its unique properties of superelasticity and shape memory. For example, nitinol is used in a number of components in minimally invasive surgery, including but not limited to catheters and stents.

[0003] While nitinol has its benefits, it also has its drawbacks. Particularly, nitinol is subject to brittle fracture. Once a fracture or crack is initiated, it is subject to propagation under fatigue conditions. This propagation could have serious consequences, especially if the nitinol is being used in a medical device placed in a patient. Another disadvantage of nitinol is that nitinol has low radiopacity, meaning that the nitinol has limited visibility when viewed by x-ray based medical imaging systems. Low radiopacity and low resistance to fatigue crack propagation limit the effectiveness of nitinol in the medical device industry.

[0004] To overcome the disadvantages, development efforts have focused on creating a ternary or higher order alloy from the base binary nitinol. Those efforts have achieved moderate improvement in nitinol properties, but the same drawbacks as with binary nitinol still exist.

SUMMARY OF INVENTION

[0005] One embodiment of the invention is an article having a nickel-titanium alloy and a homogeneous dispersion of discrete particles in the article. The discrete particles are substantially free of nickel and titanium.

[0006] In another embodiment, the article is made by melting a substantially equiatomic composition of nickel and titanium to form an alloy and dispersing at least one type of discrete particles in the alloy to form an ingot. The melting and dispersing are performed at a temperature above the alloying temperature of the composition and below the melting temperature of the discrete particles. The ingot is hot worked to form a processed ingot. The processed ingot is cold worked and annealed to form the article.

[0007] In a further embodiment, an article having a nickel-titanium alloy and a homogeneous dispersion of discrete particles substantially free of nickel and titanium is made by vacuum induction melting a substantially equiatomic composition of nickel and titanium to form a melted ingot. The melting is performed at or above an alloying temperature for the composition. During the vacuum induction melting, the discrete particles are pour stream injected into the melted ingot at a temperature below the melting point of the discrete particles. The melted ingot is hot worked to form a processed ingot. The processed ingot is cold worked and annealed to form the article.

[0008] In yet another embodiment, an article having a nickel-titanium alloy and a homogeneous dispersion of discrete particles substantially free of nickel and titanium is made by preparing an electrode having a hollow center. The electrode is made up of a substantially equiatomic composition of nickel and titanium. Inclusion particles are introduced into the hollow center. The electrode and particles are vacuum arc melted at a temperature above the alloying temperature of the composition and below the melting point of the particles to form a melted ingot. The melted ingot is hot worked to form a processed ingot. The processed ingot is cold worked and annealed to form the article.

BRIEF DESCRIPTION OF DRAWINGS

[0009] For the purpose of illustrating the invention there are shown in the drawings various forms which are presently preferred; it being understood, however, that this invention is not limited to the precise arrangements and instrumentalities particularly shown.

[0010] FIG. **1** shows an article according to one embodiment of the invention disclosed herein.

DETAILED DESCRIPTION OF INVENTION

[0011] With reference to the drawings, where like numerals identify like elements, there is shown in FIG. **1** an article **10** in accordance with the materials and methods disclosed herein. As illustrated, the article **10** is a stent. While the article is shown as a stent, the article is not so limited. The article can be all or just a portion of any structure having the elements described herein. The article can be a product including, but not limited to, actuators, hydraulic line couplings, electrical connectors, fishing lures, eyeglass frames and golf clubs. Preferably, the article is a medical device including, but not limited to, catheters, biopsy sectioning and retrieval equipment, vena cava filters, and stents.

[0012] The article **10** comprises an alloy component **12**. The alloy component comprises a nickel-titanium alloy. The nickel-titanium alloy can be a binary or higher alloy. Preferably, the nickel-titanium alloy is a binary "nitinol." Nitinol includes a family of nickel-titanium alloys having a substantially equiatomic composition of nickel and titanium. The equiatomic composition results in an ordered crystalline structure with the unique property of deformation with a high degree of recoverable (or pseudoelastic) strain, which allows the composition to be returned to its original shape after deformation.

[0013] The unique properties of nitinol are referred to as superelasticity and shape memory. Superelasticity refers to the unusual ability of certain metals/alloys to undergo large elastic deformation. When mechanically loaded, a superelastic nitinol article undergoes a recoverable deformation up to very high strains (e.g., up to 8%). The load creates a stress-induced martensitic transformation in the article. Upon unloading, a spontaneous reversal of the transformation occurs, causing the article to return to its original shape. No change in temperature is needed for the alloy to recover its initial shape.

[0014] In contrast to superelasticity, shape memory describes the characteristic that allows a plastically deformed article to be restored to its original shape by heating it. The article is heated above the austenite finish temperature of the article causing crystalline transformation and returning the article to its original shape. Shape memory is important to many nitinol-based products. For example, in the medical device industry, the shape memory property is beneficial for reusable medical instruments. Medical personnel can shape the instrument to fit the desired need (e.g., fit the patient's physiology). After use, the instrument can be heat sterilized, which results in the instrument returning to its original shape for future use.

[0015] Despite its beneficial characteristics, nitinol has low radiopacity and high susceptibility to fatigue crack propagation. Both the low radiopacity and high susceptibility to fatigue crack propagation are detrimental to the use of nitinol in products such as medical implants.

[0016] To increase radiopacity and decrease susceptibility for fatigue crack propagation, the article **10** includes a homogeneous dispersion of discrete particles **14**. As used herein, the discrete particles are any material other than nickel and titanium. Also as used herein, the discrete particles do not form an alloy with the nickel and/or titanium from the alloy component **12** of the article **10**. The discrete particles are preferably free of nickel and titanium. However, the discrete particles can be "substantially free" of nickel and titanium. Substantially free means that some diffusion from the alloy component occurs, but that the diffusion is minimal. The discrete particles can be one or more elements including, but not limited to, iridium, platinum, gold, rhenium, tungsten, palladium, rhodium, tantalum, silver, ruthenium, and hafnium. The discrete particles can be one or more alloys containing one or more elements including, but not limited to, iridium, platinum, gold, rhenium, tungsten, palladium, rhodium, tantalum, silver, ruthenium, and hafnium.

[0017] As shown in FIG. **1**, the discrete particles **14** form islands in the alloy component. The islands are substantially free of nickel and titanium and do not form alloys with the nickel and titanium of the alloy component. The islands can be formed in any geometric or non-geometric shape. Preferably, the islands are spherical in shape. The islands can be located anywhere in the article. Preferably, the islands are located such that the major axis of the discrete particles in the island are aligned perpendicular to the likely direction of fatigue crack propagation in the article.

[0018] The materials described herein provide several benefits over binary nitinol, and over nitinol alloyed with other elements to form a conventional ternary or high order alloy. For example, the discrete particles will have significantly lower impact upon the phase transformational changes of the nitinol that result in superelastic and/or shape memory effects.

[0019] Another benefit of the material is increased resistance to crack propagation. If a crack is formed in an article without particles, the crack will continue unabated thereby damaging and/or destroying the article. However, if a crack front encounters a discrete particle, further propagation will be halted, thereby preserving the integrity of the article.

[0020] If the particle is chosen from the aforementioned list of elements or alloys, then there is an additional benefit of increasing the radiopacity of the resulting system over the radiopacity of the binary nitinol alloy alone. Increased radiopacity will allow physicians or other medical personnel to view medical devices containing the material with greater clarity using x-ray based imaging techniques.

[0021] Several methods are contemplated for making the article **10**. The methods preferably produce an article having a nickel-titanium alloy and dispersion of discrete particles in the article, wherein the discrete particles are substantially free of nickel and titanium and do not form an alloy with nickel and/or titanium of the nickel-titanium alloy.

[0022] Generally, the methods include a step that includes melting a substantially equiatomic composition of nickel and titanium to form an alloy and dispersing at least one type of discrete particles in the alloy to form an ingot. The melting and dispersing are performed at a temperature above the alloying temperature of the composition and below the melting temperature of the at least one type of discrete particle.

[0023] When the Ti concentration is close to 50 weight percent, molten nitinol is highly reactive and must be melted in a vacuum. Vacuum induction melting (VIM) and vacuum consumable arc melting (VAR) are preferred ways to vacuum melt the materials.

[0024] VIM involves melting a metal composition under vacuum conditions by inducing alternating electrical eddy currents in the metal. The composition is placed in an electrically conductive crucible, preferably graphite or calcia or in a induction melter without a crucible. The composition is placed in a vacuum chamber. The composition is heated by eddy currents causing the composition to melt.

[0025] The vacuum chamber can be a furnace having an air-tight, water-cooled steel jacket that is capable of withstanding the vacuum required for melting. The inside of the furnace is typically lined with refractory materials.

[0026] VIM or vacuum skull melting (VSM) can be used in an embodiment of the presently disclosed method. In that embodiment, a substantially equiatomic composition of nickel and titanium is vacuum induction melted to form a melted ingot. The melting is performed at or above an alloying temperature for the composition. During the vacuum induction melting, particles are pour stream injected into the melted ingot. The injection is performed at a temperature below the melting point of the particles. If more than one type of particle is injected, then the temperature is below the lowest melting point of all of the particles.

[0027] Alternatively, VAR can be used in place of VIM or VSM. In such an embodiment, an electrode is prepared from a substantially equiatomic composition of nickel and titanium. The electrode is prepared having a hollow center into which particles are introduced. The particles can be introduced by injecting the particles into the hollow center, by packing a powder form of the particles into the hollow center, or any other known manner. After the particles are introduced, the electrode is vacuum arc melted to form a melted ingot. The vacuum arc melting is performed at a temperature above the alloying temperature of the composition and below the melting point of the particles.

[0028] In a further alternative, VAR can be used in conjunction with VIM or VSM. In such an alternative, VIM or VSM melting is typically preformed first, followed by VAR melting. With that order, the VIM melting creates an ingot. The ingot is then used as a consumable electrode in the VAR melting. The VIM/VAR combination combines the benefits of VIM (e.g., thorough mixing) with the benefits of VAR (e.g., high purity of the resultant alloy).

[0029] After the melted ingot is formed by any of the methods described herein, the ingot is typically refined by additional deformation processes in order to optimize the beneficial properties, such as shape memory, superelasticity, or resistance to fracture. The additional deformation is typically done by first hot working the ingot to form a processed ingot with a useful shape, while at the same time changing the microstructure in the processed ingot into one that has optimized beneficial properties. Hot working can include, for example, press forging, rotary forging, extrusion, swaging, bar rolling, rod rolling, or sheet rolling. Hot working is typically performed at temperatures in the range of 70 to 85% of the alloying temperature of the nitinol.

[0030] To further optimize the beneficial properties, the processed ingot can undergo a series of cold working steps. The cold working steps provide the final shape, surface finish, refined microstructure, and mechanical properties of the article. Preferably, cold drawing or cold rolling are used to cold work the processed ingot. Typically a cold working step is followed immediately by an annealing step. The annealing step is typically performed at about 600° C. to about 850° C. Cold working and subsequent annealing can be repeated multiple times, if necessary.

[0031] The result of each of the methods disclosed herein is an article having a nickel-titanium alloy and a homogeneous dispersion of discrete particles substantially free of nickel and titanium.

[0032] Optionally, as a finishing step, the article can be treated further by heat treatment. The heat treatment is typically done at about 450° C. to about 550° C. The heat treatment is generally necessary when, after the cold working step, the article does not fully exhibit the desired beneficial properties.

[0033] It will be appreciated by those skilled in the art that the present invention may be practiced in various alternate forms and configurations. The previously detailed description of the disclosed methods is presented for clarity of understanding only, and no unnecessary limitations should be implied therefrom.

We claim:

1. An article comprising:

a nickel-titanium alloy; and

a homogeneous dispersion of discrete particles in the article, wherein the discrete particles are substantially free of nickel and titanium.

2. An article according to claim 1, wherein the discrete particles are selected from the group consisting of iridium, platinum, gold, rhenium, tungsten, palladium, rhodium, tantalum, silver, ruthenium, and hafnium.

3. An article according to claim 1, wherein the discrete particles comprise one or more alloys substantially free of nickel and titanium.

4. An article according to claim 3, wherein the one or more alloys comprise one or more of iridium, platinum, gold, rhenium, tungsten, palladium, rhodium, tantalum, silver, ruthenium, and hafnium.

5. An article according to claim 1, wherein the discrete particles are aligned perpendicular to the likely direction of fatigue crack propagation.

6. An article according to claim 1, wherein the alloy comprises a binary alloy.

7. An article according to claim 1, wherein the alloy comprises a ternary or higher alloy.

8. An article according to claim 1, wherein the alloy is nitinol.

9. An article according to claim 1, wherein the article is a medical device.

10. An article according to claim 9, wherein the medical device is a stent.

11. A method of making an article, the method comprising:

melting a substantially equiatomic composition of nickel and titanium to form an alloy and dispersing at least one type of discrete particle in the alloy to form an ingot, wherein the melting and dispersing are performed at a temperature above the alloying temperature of the composition and below the melting temperature of the discrete particles;

hot working the ingot to form a processed ingot; and

cold working and annealing the processed ingot to form the article.

12. A method of making an article, the method comprising:

vacuum melting a substantially equiatomic composition of nickel and titanium to form a melted ingot, wherein the melting is performed at or above an alloying temperature for the composition;

pour stream injecting particles into the melted ingot during vacuum induction melting at a temperature below the melting point of the particles;

hot working the melted ingot to form a processed ingot; and

cold working and annealing the processed ingot to form the article, the article comprising a nickel-titanium alloy and a homogeneous dispersion of discrete particles substantially free of nickel and titanium.

13. A method of making an article according to claim 12, wherein the substantially equiatomic composition has a nickel:titanium atomic ratio of about 50:50.

14. A method according to claim 12 wherein the particles are selected from the group consisting of iridium, platinum, gold, rhenium, tungsten, palladium, rhodium, tantalum, silver, ruthenium, and hafnium.

15. A method according to claim 12, wherein the particles comprise an alloy comprising one or more of iridium, platinum, gold, rhenium, tungsten, palladium, rhodium, tantalum, silver, ruthenium, and hafnium.

16. A method according to claim 12, wherein the vacuum melting comprises vacuum induction melting.

17. A method according to claim 12, wherein the vacuum melting comprises vacuum skull melting.

18. A method of making an article, the method comprising:

preparing an electrode having a hollow center, the electrode comprising a substantially equiatomic composition of nickel and titanium;

introducing particles into the hollow center;

vacuum arc melting the electrode and the particles at a temperature above the alloying temperature of the composition and below the melting point of the particles to form a melted ingot;

hot working the melted ingot to form a processed ingot; and

cold working and annealing the processed ingot to form the article, the article comprising a nickel-titanium alloy and a homogeneous dispersion of discrete particles substantially free of nickel and titanium.

19. A method according to claim 18, wherein the particles are selected from the group consisting of iridium, platinum, gold, rhenium, tungsten, palladium, rhodium, tantalum, silver, ruthenium, and hafnium.

20. A method according to claim 18, wherein the particles comprise an alloy comprising one or more of iridium, platinum, gold, rhenium, tungsten, palladium, rhodium, tantalum, silver, ruthenium, and hafnium.

21. A method according to claim 18, wherein the particles are introduced by injecting the particle into the hollow center.

22. A method according to claim 18, wherein the particles are introduced by packing a powdered particle into the hollow center.

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