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[54] **MANUFACTURE OF A TWO-WAY SHAPE MEMORY ALLOY AND DEVICE**

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### FOREIGN PATENT DOCUMENTS

143580	6/1985	European Pat. Off. .
0625153	8/1993	WIPO .

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[52] **U.S. Cl.** ..... **148/510; 148/563; 606/198**

[58] **Field of Search** ..... **148/510, 511,**  
**148/563; 606/195, 198, 200; 623/1, 12**

### [57] ABSTRACT

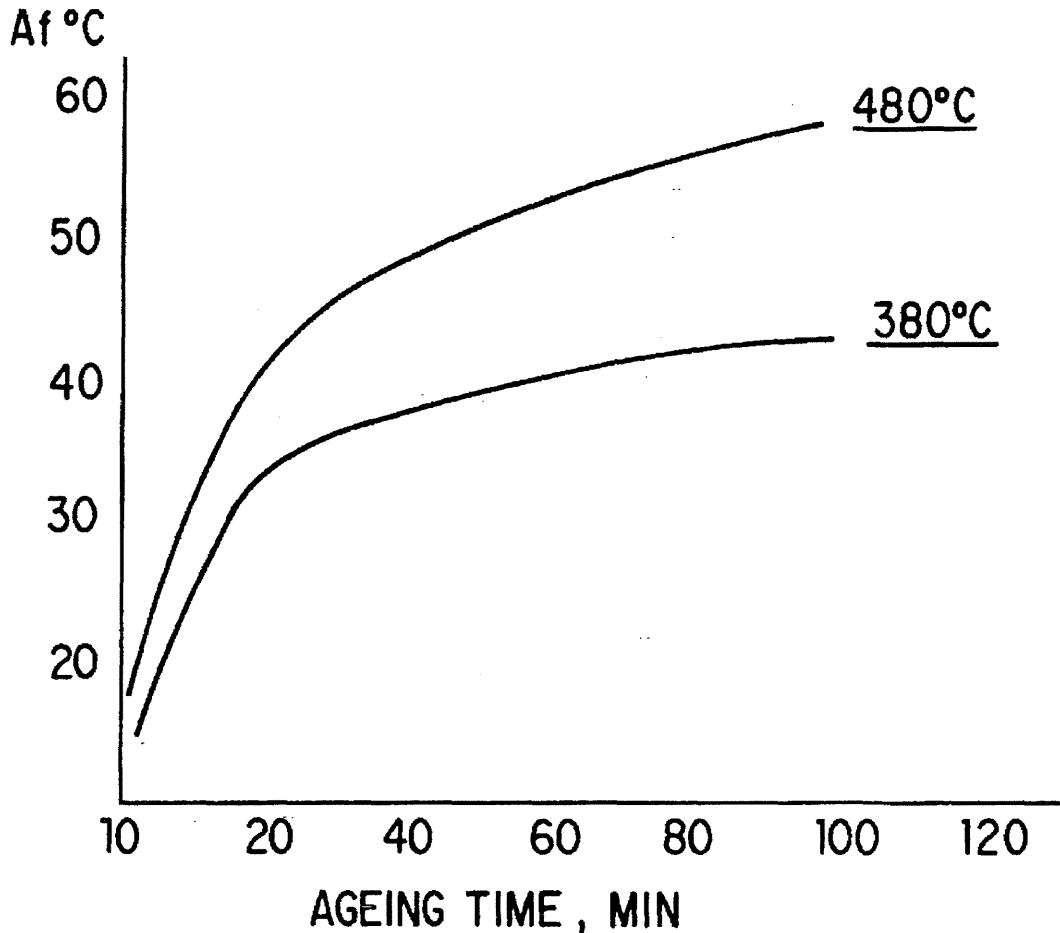
A process is provided for the manufacture of a two-way shape memory alloy and device. The process of the invention allows a reversible adjustment of the characteristic transformation temperatures, as well as the direction of the two-way shape memory effect, at the final stage of manufacture.

### [56] References Cited

#### U.S. PATENT DOCUMENTS

4,665,906	5/1987	Jervis .....	606/108
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**15 Claims, 1 Drawing Sheet**



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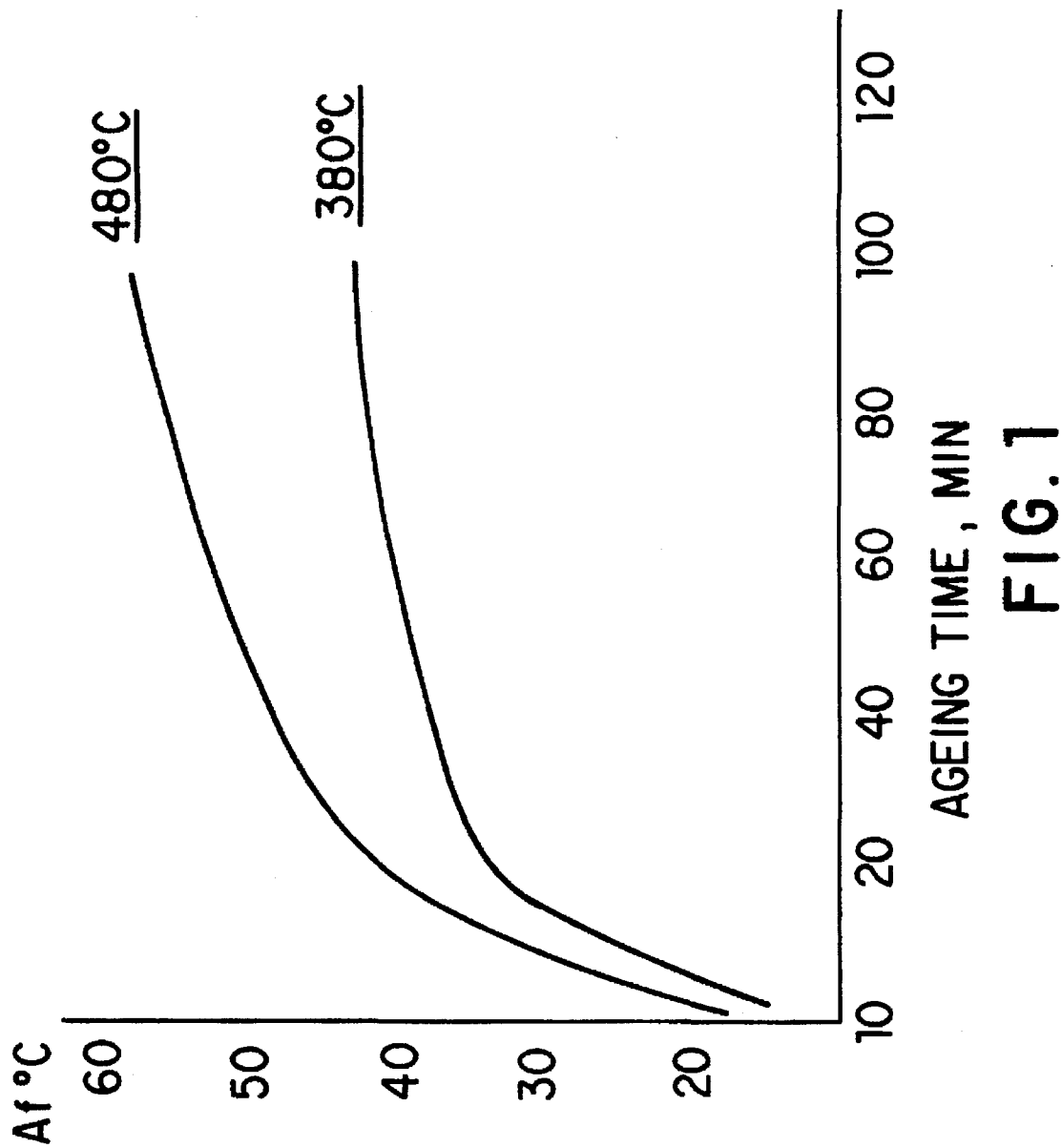


FIG. 1

## MANUFACTURE OF A TWO-WAY SHAPE MEMORY ALLOY AND DEVICE

### FIELD OF THE INVENTION

The present invention generally relates to shape memory alloys (SMA) i.e. alloys which can switch from one shape to another, "memorized" state upon a change in temperature. More specifically, the present invention relates to an SMA which is nickel-titanium based, also known as Nitinol.

### BACKGROUND OF THE INVENTION

Various metal alloys possess the ability to change their shape as a result of a change in temperature. Such SMA can undergo a reversible transformation from a martensitic state, in which the material is relatively soft and deformable, to an austenitic state in which the material possesses super elastic properties and is relatively firm. The transformation from the martensitic state to the austenitic state will be referred to herein as the "austenitic transformation", and the other transformation, from the austenitic state to the martensitic state, will be referred to herein as the "martensitic transformation". The austenitic transformation occurs over a range of temperature which is higher than the range of temperatures in which the reverse transformation occurs. This means, that once transformed to an austenitic state, an SMA will remain in that state even when cooled to a temperature below that in which the austenitic transformation began, as long as the temperature is above that in which the martensitic transformation begins.

A particular class of SMAs are alloys of nickel and titanium—Nitinol. Nitinol has found a variety of uses in medical as well as other fields. Medical uses of SMAs, particularly Nitinol, has been described in U.S. Pat. Nos. 4,665,906, 5,067,957, European Patent Application 143,580, U.S. Pat. No. 4,820,298 and many others.

For medical uses it is usually desired that the alloy will undergo an austenitic transformation over a narrow, well defined range. For example, a vascular stent of the two-way SMA type, such as that described in European Patent Application, Publication No. 625153, is typically deployed in the body while being in the martensitic state at body temperature, and then after heating, it transforms into the austenitic state, and then remains in the austenitic state when cooled to the body temperature. It can be appreciated that if excessive heating to transform the SMA from the martensitic to the austenitic state is required, this can be damaging to the surrounding tissue and is thus undesirable. Thus, it would ideally be desired that the austenitic transformation will begin at a temperature several degrees above body temperature and will be over a temperature range which will not cause tissue damage owing to the excessive heating.

### GENERAL DESCRIPTION OF THE INVENTION

It is an object of the present invention to provide a process for the treatment of a Nitinol alloy to obtain an alloy with a two-way shape memory effect (SME).

It is more specifically an object of the invention to provide such a process to obtain a two-way SME which does not require a multi-cycle "training" to yield a two-way SME.

It is still further an object of the invention to provide a process to obtain a two-way SME, with a narrow range of temperatures over which the austenitic transformation occurs.

In accordance with the invention two embodiments are

times as the "first embodiment", the process yields an alloy with a direction of the austenitic and the martensitic transformations dictated by the direction of a conditioning transformation in the martensitic state. In accordance with another embodiment of the invention, to be referred to herein at times as the "said second embodiment", the process yields an alloy with a direction of a martensitic or austenitic transformations which is independent on the deformation introduced in the martensitic state.

In the following description and claims the term "Nitinol" will be used to denote an alloy comprising primarily nickel and titanium atoms. A Nitinol alloy has typically the following empiric formula:



wherein A represents Ni, Cu, Fe, Cr or V

l, m, and n representing the proportions of the metal atoms within the alloy, the value of l, m and n being about as follows:

$$l=0.5$$

$$m=0.5-n$$

$$n=0.003 \text{ to } 0.02.$$

In accordance with the invention, there is provided a process for treating a raw Nitinol alloy having an initial form to obtain an alloy with a final form in which it exhibits a two-way shape memory effect (SME) whereby it has an austenitic and a martensitic memory state with associated austenitic and martensitic shapes, respectively, the process comprising the steps of:

(a) heating a sample of the raw Nitinol alloy, to a temperature of about 450°–550° C. for about 0.5–2.5 hours, and then testing the sample for temperature difference between  $A_s$  and  $A_f$ , wherein  $A_s$  is a temperature wherein austenitic transformation, namely transformation between the martensitic to the austenitic state, begins, and  $A_f$  is a temperature where the austenitic transformation ends;

(b) subjecting the raw Nitinol alloy to a first heat treatment based on the  $A_f-A_s$  difference obtained in step (a), as follows:

where the difference is less than about 7° C., heat treating the alloy to a temperature of about 450°–500° C. for about 0.5–1.0 hours;

where the difference is more than about 7° C., heat treating the alloy to a temperature of about 510°–550° C. for about 1.0–2.5 hours;

(c) subjecting the alloy to thermo-mechanical treatment, comprising plastic deforming the alloy at a strain rate, of less than 5 sec<sup>-1</sup>, with simultaneous internal heating of a portion of the alloy where the deformation occurs to a temperature of about 250°–550° C., the deformation of this step being less than 55%, preferably less than 40%;

(d) if the deformation in step (c) did not yield the final form, subjecting the alloy to an intermediate heat treatment at a temperature of about 500°–550° C., for about 0.5–2 hours, and then repeating step (c); and

(e) subjecting the alloy to a final heat treatment and to a memorizing treatment.

The particulars of the final heat treatment and the memorizing treatment, are different in said first embodiment and in second embodiment. In accordance with said first embodiment, this treatment comprises:

(i) forming the alloy into the form to be assumed by it in

- (ii) subjecting the alloy to a polygonization heat treatment at about 450°–550° C. for about 0.5–1.5 hours, then to solution treatment at about 600°–800° C. for about 2–50 mins., and then to an aging treatment at about 350°–500° for about 0.15–2.5 hours,
- (iii) deforming the alloy to assume a conditioning form, the deformation being less than about 15%, and preferably less than 7%, and being performed at a temperature T, which meets the following formula

$$T < M_s + 30^\circ \text{ C.}$$

wherein  $M_s$  is a temperature where the martensitic transformation begins, and then heating the alloy to a temperature of or above that in which the austenitic transformation of the alloy ends;

whereby the alloy is conditioned to memorize an austenitic state in which it has deformed into which it was formed under (i) above, and an austenitic state, in which it has a martensitic form with an intermediate degree of deformation between the austenitic form and the conditioning form.

It should be pointed out that also a single cycle of deformation in step (e) (iii) is usually sufficient, it may at times be desired to repeat this cycle one or more times.

In accordance with said second embodiment, the final heat and memorizing treatment comprises:

- (i) forming the alloy into a form other than the form to be assumed by it in the austenitic state,
- (ii) subjecting the alloy to a heat treatment at about 450°–500° C. for about 0.5–2 hours, then subjecting the alloy to polygonization and solution treatment at about 600°–800° C. for about 2–50 mins., and then subjecting the alloy to aging treatment at about 350°–500° C. for about 0–2 hours,
- (iii) forming the alloy into a form to be assumed by it in the austenitic state,
- (iv) subjecting the alloy to a memorizing heat treatment at about 500°–600° C. for more than about 10 mins., and then subjecting the alloy to aging treatment at about 350°–500° C. for about 0.15–2.5 hours;

whereby the alloy is conditioned to memorize an austenitic state in which it has an austenitic form assumed by it in (iii) above, and a martensitic state, wherein it has a martensitic form being a form with an intermediate degree of deformation between the form in which the alloy was formed in (i) above and the austenitic form.

Following the treatment in accordance with both said first and said second embodiments,  $A_f$  will be between about 10 to about 60° C. In order to increase  $A_f$  and  $A_s$ , the alloy may then be subjected to aging heat treatment at a temperature of about 350°–500° C. In order to decrease  $A_f$  and  $A_s$ , the alloy can then be subjected to a solution treatment at a temperature of about 510° to about 800° C.

By differential aging or solution treatment in different portions the alloy will have different temperatures of austenitic transformation. This is as time desired, for example, in the case of a medical stent, to have portions thereof with different transition temperatures of austenitic transformation and/or martensitic transformation.

By the above process, SMAs for a variety of applications may be prepared. Particularly preferred in accordance with the invention are SMAs useful as medical devices. Examples are various orthopaedic devices and medical stents. A stent made of an SMA prepared by the above process, is a particularly preferred example in accordance with the invention. A process for the preparation of such medical devices also form an aspect of the invention.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 in the drawings shows the relation between  $A_f$  and the aging time, in different aging temperatures.

#### DETAILED DESCRIPTION OF THE INVENTION

The temperature range over which the austenitic transformation takes place, is critical in a variety of medical applications. A specific case in point are medical stents such as those made of a two-way SMA described in European Patent Application No. 626153. Such a medical stent, is deployed in a tubular organ at body temperature, and then heated so as to allow the occurrence of the austenitic transformation. Once heated, it remains in the austenitic state in body temperature and supports the wall of the tubular organ. Such medical stents are designed so that the beginning of the austenitic transformation will occur at a temperature at or above 40° C. It will however be appreciated, that the range of temperature over which the austenitic transformation occurs should desirably be narrow since excessive heating where the temperature range is large, can cause tissue damage. Furthermore, a narrow temperature range will generally ensure also a more rapid transition from the martensitic to the austenitic states.

In the following description the invention will be described at times with particular reference to its application for the preparation of medical stents with a narrow range of austenitic transformation. It will however, be appreciated, that the invention is not limited thereto and the application of the invention to the preparation of medical stents is exemplary only. In accordance with the present invention, a raw Nitinol alloy, which is typically provided by manufacturers in the form of a wire, is first tested for the difference between  $A_s$  and  $A_f$ . For this purpose a small sample of the material is taken. Based on the  $A_s$ – $A_f$  difference, the alloy, e.g. the wire, is then subjected to a first heat treatment.

Following the first heat treatment, the alloy is subjected to a thermo-mechanical treatment where the alloy is simultaneously heated and subjected to a mechanical deformation. In the case of a process intended for the manufacture of a medical stent, the mechanical deformation typically involves changing the form of the alloy, from an initial form of a wire, to that of a ribbon or band; or alternatively, changing the wire into a wire of a smaller diameter. In order to retain the shape memory effect (SME) of the alloy, the total degree of deformation during the mechanical treatment, should be less than 55%, preferably less than 40%. Where the total required eventual deformation is more than 55%, the thermo-mechanical treatment is repeated following an intermediate heat treatment.

The thermo-mechanical treatment particularly where the alloy is processed to be used as a medical stent, is typically warm rolling, with the heating of the deforming portions being a result of electro-stimulation at a preferred current density of about 500–2000 A/cm<sup>2</sup>. A big advantage of such a treatment is that in addition to causing a mechanical deformation, it leads also to heating of the pre-cracks with a high dislocation density owing to the relatively high electrical resistance at such pre-cracks which gives rise to a selective overheating at such points and heating of the pre-cracks. Moreover, electro-stimulated warm thermo-mechanical treatment at the above current density accelerates dislocation reaction, which results in a perfect dislocation subgrain structure formation. Furthermore, the heating electrical current gives rise to a dynamic aging process with a second phase precipitation on the walls of the subgrain



dislocation cells. This structure provides for a very narrow thermal interval of austenitic transformation  $A_f-A_s$  for the shape memory alloy, and for a variety of other advantageous properties to be explained below.

In an electrically stimulated warm rolling, where the current density decreases below  $500 \text{ A/cm}^2$ , or the strain rate of the deformation is above about  $5 \text{ sec}^{-1}$ , there is an increase of the random dislocation density which will decrease the degree of perfection of the subgrain structure. For a narrow  $A_f-A_s$  interval, a subgrain structure as perfect as possible is required. Accordingly, with an increase in the random dislocation density there is an increase in the  $A_f-A_s$  interval. For example, where the current density is about  $400 \text{ A/cm}^2$ , or where strain rate is about  $8 \text{ sec}^{-1}$ , the  $A_f-A_s$  interval after final heat treatment will be about  $10^\circ-12^\circ \text{ C}$ . Furthermore, increasing of the current density to above about  $2000 \text{ A/cm}^2$ , leads to a recrystallization process, that prevents formation of the necessary subgrain cells with precipitation on the cell walls.

The memorizing treatment involves a conditioning step in which microscopic changes within the alloy condition it to "memorize" the two forms which the alloy assumes during its use, that in the martensitic state ("martensitic form") and that in the austenitic state ("austenitic form").

In accordance with said first embodiment, the alloy is formed into a shape to be assumed by it in the austenitic state, e.g. in the case of a stent this involves winding on a mandrel having a diameter of a stent in the austenitic state. The alloy is then typically placed in a vacuum or inert atmosphere furnace, in which it is first subjected to a memorizing and internal structure polygonization treatment, at a temperature of about  $450^\circ-550^\circ \text{ C}$ . for about 0.5–1.5 hours, and then heated to about  $600^\circ-800^\circ \text{ C}$ . for about 2–50 mins. During this latter heating, the alloy undergoes a solution treatment with re-arrangement of dislocations which are freed after solution treatment. Subsequently, the alloy is subjected to a final aging treatment at a temperature of about  $350^\circ-500^\circ \text{ C}$ . for about 0.15–2.5 hours.

The result of the above treatment is a subgrain structure which imparts the alloy with several features. For one, the temperature of the austenitic transformation,  $A_f$  can be adjusted within a range of  $10^\circ-60^\circ \text{ C}$ . with a very narrow interval of  $A_f-A_s$  of about  $1-5^\circ \text{ C}$ .

In case it is desired to decrease  $A_f$ , the alloy may be subjected to a solution treatment at a temperature of about  $510^\circ-800^\circ \text{ C}$ . In order to achieve a desired  $A_f$ , both the temperature as well as the aging time can be controlled. For example, where the Nitinol alloy has after the final heat treatment an  $A_s$  of about  $45^\circ \text{ C}$ . and an  $A_f$  of about  $48^\circ \text{ C}$ ., after a solution treatment at  $640^\circ \text{ C}$ . for about 5 mins., the  $A_s$  and  $A_f$  decrease to about  $23^\circ \text{ C}$ . and  $27^\circ \text{ C}$ ., respectively; following solution treatment at  $640^\circ \text{ C}$ . for 10 mins.,  $A_s$  and  $A_f$  decrease to about  $11^\circ \text{ C}$ . and  $15^\circ \text{ C}$ ., respectively.

In order to increase  $A_f$ , the alloy is subjected to an aging heat treatment at a temperature of about  $350^\circ-500^\circ \text{ C}$ . Here again, in order to achieve a desired  $A_f$ , both the temperature as well as the aging time can be controlled. This is demonstrated, for example, in FIG. 1 which gives the relation between the aging time at two different temperatures ( $380^\circ \text{ C}$ . and  $480^\circ \text{ C}$ .) and the resulting  $A_f$  following a solution treatment at  $640^\circ \text{ C}$ . for 20 mins. As can be seen, for example, aging treatment at  $380^\circ \text{ C}$ . for about 100 mins. yields an  $A_f$  of about  $40^\circ \text{ C}$ ., with the same  $A_f$  being reached with an aging treatment at  $480^\circ \text{ C}$ . of about 40 mins. Aging at a temperature of about  $450^\circ \text{ C}$ . for about 80 mins. will yield an  $A_s$  of about  $46^\circ \text{ C}$ . and an  $A_f$  of about  $49^\circ \text{ C}$ . (not

A unique feature of the process of the invention is the fact that the two-way SME is induced by only one cycle of deformation. In the case of a first embodiment of the invention, this is achieved by deforming the alloy into a conditioning form at a temperature of  $T < M_s + 30^\circ \text{ C}$ . followed by heating to a temperature at or above the  $A_f$  of the alloy. The deformation should be less than 15% and preferably less than 7%. A deformation above 15% will effect the internal structure of the material and yield a total or partial loss of the memory form of the austenitic state. A deformation between 7% and 15% will have only such a partial harming effect. The martensitic memory form which the alloy assumes after the above conditioning step, is an intermediate form between the austenitic memory form and the conditioning form. The direction of the two-way SME following such memorizing treatment, coincides with the direction in the martensitic state deformation. For example, where a deformation in the martensitic state involves a decrease in diameter, the diameter of the alloy in the martensitic state will be less than that of the austenitic state, and vice versa.

Generally, the process in accordance with said first embodiment allows a reversible adjustment of the characteristic transformation temperatures as well as the direction of the two-way SME at the final stage of manufacture.

A final memorizing treatment in accordance with the second embodiment of the invention, gives rise to a two-way SME without the need for a final deformation to induce the two-way SME. This effect is not determined when indirect SME occurs. The second embodiment is particularly useful for the manufacture of a stent with a two-way SME, and the description below will refer to this specific embodiment. The Nitinol ribbon or wire is wound on a mandrel having a diameter equal to  $2R_1$  constrained and placed into a vacuum furnace, at a temperature of about  $450^\circ-550^\circ \text{ C}$ . for about 0.5–1.5 hours, so that internal structure normalization and textural formation takes place. Similarly as above, the alloy is then subjected to solution treatment and structure improvement at a temperature of  $600^\circ-800^\circ \text{ C}$ . for 2–50 mins. and then to an ageing treatment at  $350^\circ-500^\circ \text{ C}$ . for 0.15–2.5 hours. The ribbon or wire is then rewound on a mandrel with a diameter  $2R_2$ , which is the diameter to be assumed by the stent in the austenitic state and then subjected to a memorizing and ageing treatment at temperature of  $450^\circ-550^\circ \text{ C}$ . for 0.15–2 hours. If the strain of this treatment  $\epsilon_{\text{treat.}} = \frac{1}{2}w(1/R_2 - 1/R_1) < 0$  ( $w$  being the thickness in case of a ribbon and the diameter in case of a wire) the corresponding strain of the two-way SME during cooling  $\epsilon_{\text{m.}} = \frac{1}{2}w(1/R_{\text{m.}} - 1/R_2) > 0$  ( $R_{\text{m.}}$  being the diameter of the stent when assuming its martensitic state) and vice versa. As a result of this treatment, there is a very narrow temperature range in which the austenitic transformation takes place,  $A_f-A_s = 1^\circ-5^\circ \text{ C}$ ., with a possibility to change  $A_f$  between  $10^\circ$  and  $60^\circ \text{ C}$ ., similarly as above.

The two-way SME in cooling may either coincide or oppose the direction of the deformation in the martensitic state. In case  $R_2$  is larger than  $R_1$ , and  $R_{\text{m.}}$  will be smaller than  $R_2$ , the device shrinks when it is cooled. In case  $R_2$  is less than 0, i.e. a reverse bending, and  $R_2$  is larger than  $R_{\text{m.}}$ , the device will expand when cooled.

Finally, another result of the process of the present invention is a high resistance of the formed alloy, to pitting corrosion and hydrogen embrittlement which may occur in the biological media with their relatively high chlorine ion content.

The invention will now be illustrated further by several

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