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(54) **Title:** SHAPE MEMORY MATERIAL AND METHOD OF MAKING THE SAME

(57) **Abstract:** The present invention relates generally to a shape memory and/or super-elastic material, such as a nickel titanium alloy. Additionally or alternatively, the present invention relates to a super-elastic or pseudo-elastic material that has an initial transition temperature A_f above a body temperature. The shape memory material can have a super-elasticity or pseudo-elasticity property at a temperature below the initial transition temperature A_f of the material. For example, the shape memory material can have its workable temperature for producing super-elasticity or pseudo-elasticity of about 0°C to 15°C below the initial transition temperature A_f. The shape memory material can be malleable at a room temperature, and become super-elastic or pseudo-elastic at a body temperature. In addition, the present invention relates to a method of making a shape memory or a super-elastic material. The treatment protocols can include but not limited to thermo-mechanical, thermo-mechanical, radiation, and ternary alloying treatments.

SHAPE MEMORY MATERIAL AND METHOD OF MAKING THE SAME

CROSS-REFERENCE TO RELATED APPLICATION

This patent application claims benefit of U.S. Provisional Patent Application No. 60/464,083 filed April 18, 2003.

TECHNICAL FIELD

The present invention relates generally to a shape memory material. More specifically, the present invention relates to a super-elastic or pseudo-elastic material that has an initial transition temperature A_f above a body temperature. In addition, the present invention relates to a method of making the shape memory material.

BACKGROUND OF THE INVENTION

Nickel titanium (NiTi) alloys have the properties of shape memory effect and superelasticity. The shape-memory phenomenon, first found nearly half a century ago, is that a material can exhibit one shape at a cold temperature and another shape after being heated to a higher temperature. The material is in its original shape at the higher temperature. When being cooled to a lower temperature, the material retains its original shape but changes the structure to martensite, where the material can be easily deformed into different shapes at the lower temperature. Upon heating, the material changes back to austenite, where the deformation is recovered and the shape is restored (one-way shape memory). Alloys can also have two memories (two-way shape memory) that exhibit a reversible effect, with heat causing the change in shape which can be reversed by cooling. The phase that is stable at the lower temperature is called Martensite (B19'); the phase stable at the higher temperature is called Austenite (B2).

The shape memory effect (SME) results from thermoelastic martensitic transition. Martensite is produced when austenite crystals in the parent matrix are cooled below the martensitic phase transition starting temperature (M_s). No macro shape change occurs at this stage, because of the formation of martensite twin in a self-accommodation structure. Twin boundaries can move and disappear when the martensite gains increased stress at a temperature below the martensitic phase transition finishing temperature (M_f), leading to macro deformation. The deformed martensite can be restored to the original shape of the parent phase through reverse transformation (from martensite to austenite) when being heated to a temperature above the austenitic phase transition starting temperature (A_s). Sometimes, martensitic reorientation can occur if the martensitic phase in the matrix is under increased stress. This phenomenon greatly contributes to the shape memory effect.

Super-elasticity (SE) or pseudo-elasticity (PE) occurs when a shape memory alloy shows a good performance at a temperature above the austenitic phase transition finishing temperature A_f and is deformed at a temperature above M_s. For example, the best workable temperature range for PE is 10°C to 15°C above the A_f. This effect is caused by the stress-induced martensite (SIM) formed at a temperature above M_s. As martensite is formed with stress applied thereto, the martensite reverts immediately to the undeformed austenite when the stress is removed. This process produces a "rubber-like" behavior in these alloys. This material will show two plateaus on the stress-strain curve in a tensile or compression testing, one in the upper (loading) section and the other in the lower (unloading) section, which are the regions of superelasticity.

<u>SUMMARY OF THE INVENTION</u>

The present invention can provide a shape memory material that has its workable temperature range of super-elasticity of about 0°C to 15°C below the initial transition temperature A_f of the material. For example, the shape memory material can be a heat-treated NiTi alloy. The physical properties of the shape memory material are such that the material is malleable at room temperature, but becomes super-elastic or pseudo-elastic at a body temperature. The shape memory material can be used in various applications, including but not limited to, orthopedic implants.

The present invention can also provide a method of making a shape memory material. The method can comprise treating a raw material at a temperature ranging from about 700°C to 900°C for a time period of about 0.5 to 2 hours. The heat-treated raw material can be cooled by various means, such as by air or water or inside furnace. The treated raw material can be subjected to an ageing treatment at a temperature ranging from about 200°C to about 520°C for a time period of about 0.25 to 2 hours to provide a shape memory material. The shape memory material can be cooled by various means, such as by air or water or inside furnace.

Optionally, the method can comprise a second ageing treatment of the material at a temperature ranging from about 200°C to about 500°C for a time period of about 0.5 to 2 hours followed by a cooling process, such as by air or water or inside furnace.

BRIEF DESCRIPTION OF THE DRAWINGS

The detailed description of the present invention will be better understood in conjunction with the accompanying drawings, which are for illustrative purposes only. The present invention is not limited to the exemplary embodiments shown in such drawings.

Fig. 1 shows various thermal treatment protocols for adjusting the initial transition temperature A_f of the solid solution to be above a body temperature.

Fig. 2 shows various protocols of a second ageing treatment of the solid solution.

Fig. 3 shows various alternative protocols of a second ageing treatment of the solid solution.

Fig. 4 shows the mechanical testing result of Specimen No. 5 having super-elasticity at a human body temperature (e.g., 96°F to 99°F).

DETAILED DESCRIPTION OF THE INVENTION

For the purposes of promoting an understanding of the principles of the present invention, various exemplary embodiments will be illustrated and discussed in great details in connection with the accompanying drawings. In particular, various thermal treatment protocols will be discussed, which facilitate to utilize or maximize the super-elasticity or pseudo-elasticity of the shape memory material, such as a nickel titanium alloy, at a human body temperature.

The present invention can provide a new material, which can have a shape memory effect. The shape memory effect enables a material to return to a predetermined shape upon heating or cooling via a phase transformation. For example, the material can have a shape memory effect at a body temperature, such as a human body temperature. Additionally or alternatively, the present invention can provide a new material, which can have a super-elasticity or pseudo-elasticity property. The super-elastic or pseudo-elastic property of a material means that a constant force or similar forces can be obtained when the material is mechanically or physically deformed beyond its elastic limit but within its plastic limit. Such a force can be kept constant or substantially constant during the deformation process. For example, the material can have a super-elasticity or pseudo-elasticity at a body temperature, such as a human body temperature.

In one exemplary embodiment, the shape memory material can have an initial transition temperature A_f above a body temperature, such as a human body temperature. For example, the normal range of human body temperature is in the range of about 36.1°C to about 37.8°C. In an exemplary embodiment, the material can have an initial transition temperature A_f in the range of about 36°C to about 72°C. In an exemplary embodiment, the material can have an initial transition temperature A_f of about 0°C to about 15°C above a body temperature, without any stress loading to the material. For example, the material can have an initial transition temperature A_f in the range of about 36°C to about 53°C. In another exemplary embodiment, the material can have an initial transition temperature A_f of about 10°C to about 15°C above a body temperature. For example, the material can have an initial transition temperature A_f in the range of about 46°C to about 53°C.

In another embodiment, the present invention can provide a material with a super-elasticity or pseudo-elasticity property. In an exemplary embodiment, the material can have a super-elasticity or pseudo-elasticity at a body temperature. In another exemplary embodiment, the material can be malleable at a room temperature but change to a super-elasticity or pseudo-elasticity phase at a human body temperature.

The material can have various forms and/or compositions. For example, the material can be in the form of an alloy. In an exemplary embodiment, the material can comprise a nickel titanium alloy. In another exemplary embodiment, the material can comprise an equiatomic nickel titanium alloy, such as having a nickel to titanium ratio of about 50% to 50%. It will be appreciated that other forms and/or compositions of the material are also within the scope of the present invention.

According to another aspect of the present invention, various articles can be formed of the shape memory and/or super-elastic material. For example, the articles can be structural components of various shapes, such as rod, cylindrical, square, hexagonal, or other shapes or a combination of above shapes. Additionally or alternatively, the shape memory and/or super-elastic material can have various applications, including but not limited to, various medical uses such as orthopedic implants. For example, the shape memory material and/or the nickel titanium alloy can be made into various plates, rods, wires, screws, or a combination of the above as implants to be applied to a patient's bone or other tissues or organs. It will be appreciated that other applications of the shape memory and/or super-elastic material are also within the scope of the present invention.

In one embodiment, the article or structural component formed of the shape memory and/or super-elastic material can have shape memory property and/or super-elasticity. For example, the article or structural component can be super-elastic and capable of providing a substantially constant or similar forces. In an exemplary embodiment, the article can be in the form of a medical implant and provide a constant force for bone fixation. In one exemplary embodiment, such constant force can be determined or controlled in various ways to reinforce or reduce the force generated by the material. For example, the constant force can be determined by the size or number of the article used, the composition of the material, thermal treatment, thermal mechanical treatment, ternary alloying, radiation treatment of the material, and any combination of the above. It will be appreciated that other treatments for determining or controlling the constant force are also within the scope of the present invention.

According to a further aspect of the present invention, a method can be provided for making a shape memory and/or super-elastic material. For example, one or more of thermal treatment, thermal-mechanical treatment, radiation, ternary alloying, and the like can be used. In an exemplary embodiment, a thermal treatment can be used to form the shape memory and/or super-elastic material. It will be appreciated that various other treatments and/or combinations of treatments are also within the scope of the present invention. Optionally, one or more additional mechanical treatments, such as compression, tensile, bending, torsion, cold working, hot working, and the like can be used for making the shape memory and/or super-elastic material.

In one embodiment, the method can comprise a solid solution treatment and an ageing treatment of a raw material. In an exemplary embodiment, the raw material can be any alloy, such as a nickel titanium alloy. In a solid solution treatment, the raw material can be heated to a temperature near the crystallization temperature of the raw material. The elevated temperature can cause atomic diffusion, recrystallization, and/or precipitation. The treated material can be subjected to cooling by various conventional methods and/or the ageing treatment to form the shape memory material having an initial transition temperature A_f above a body temperature.

In one exemplary embodiment, the solid solution treatment of the raw material can be carried out at a temperature ranging from about 700°C to about 900°C. In an exemplary embodiment, the raw material is treated at a temperature ranging from about 800°C to about 900°C. In another exemplary embodiment, the raw material is treated at about 800°C. Additionally or alternatively, the solid solution treatment can last for a time period of about 0.5 to 2 hours. It will be appreciated that various other embodiments of the solid solution treatment are also within the scope of the present invention.

In another exemplary embodiment, the treated raw material can be cooled by various conventional methods, such as by air or water or inside furnace. For example, the treated raw material can be quenched by water. It will be appreciated that various other embodiments of the cooling treatment are also within the scope of the present invention.

In a further exemplary embodiment, the ageing treatment of the treated raw material can be carried out at a temperature ranging from about 200°C to about 520°C to obtain the shape memory or super-elastic material. In an exemplary embodiment, the ageing treatment can be carried out at a temperature ranging from about 250°C to about 500°C. Additionally or alternatively, the ageing treatment is carried out for a time period of about 0.25 to 2 hours. In an exemplary embodiment, the ageing treatment is carried out for a time period of about 0.5 to 2 hours. It will be appreciated that various other embodiments of the ageing treatment are also within the scope of the present invention.

Optionally, a second ageing treatment can be provided to reinforce the super-elasticity or pseudo-elasticity of the shape memory material. In an exemplary embodiment, the second ageing treatment can be carried out at a temperature from about 200°C to about 500°C. In another exemplary embodiment, the second ageing treatment can be carried out at a temperature from about 250°C to about 500°C. Additionally or alternatively, the second ageing treatment can be carried out for about 0.5 to 2 hours. In an exemplary embodiment, the second ageing treatment can be carried out for about 0.5 to 1 hour. It will be appreciated that various other embodiments of the second ageing treatment are also within the scope of the present invention.

The present invention can further provide a material formed according to the above method. In an exemplary embodiment, the material can have an initial transition temperature A_f above a body temperature. For example, the material can have an initial austenite phase finishing temperature of about 0°C to 15°C above a body temperature. In one exemplary embodiment, the material can comprise a nickel titanium alloy. For example, the NiTi alloy can have a nickel to titanium ratio of about 50% to 50%.

Fig. 1 illustrates various exemplary thermal treatment protocols, where the solid solution temperature, ageing temperature, time for treatment and cooling method are shown. In addition, the austenite phase starting temperature, peak temperature, and finish temperature of each specimen are also shown. In one exemplary embodiment, Specimen No. 5 can be treated at the temperature of about 800°C for about one hour. The solid solution so treated can be cooled inside furnace. The treated solid solution can be subjected to an ageing treatment at the temperature of about 450°C for about half an hour and then be quenched by water. The material so formed can have an initial austenite phase starting temperature of about 26°C, an initial austenite phase peak temperature of about 33.5°C, and an initial austenite phase finish temperature of about 47°C.

In another exemplary embodiment, Specimen No. 7 can be treated at the temperature of about 800°C for about one hour and cooled inside furnace. The treated solid solution can be subjected to an ageing treatment at about 450°C for about 0.75 hour and quenched by water. The resulting material can have an initial austenite phase starting temperature of about 16°C, an initial austenite phase peak temperature of about 22.5°C, and an initial austenite phase finish temperature of about 44°C.

In a further exemplary embodiment, Specimen No. 14 can be treated at the temperature of about 800°C for about one hour and cooled down inside furnace. The treated solid solution can be subjected to an ageing treatment at the temperature of about 500°C for about half an hour and then cooled inside furnace. The material so formed can have an initial austenite phase starting temperature of about 12°C, an initial austenite phase peak temperature of about 32°C, and an initial austenite phase finish temperature of about 43°C.

Figs. 2 and 3 show various alternative thermal treatment protocols. For example, various Specimen Nos. 20 to 40 can be first subjected to a thermal treatment protocol, such as one of those shown in Fig. 1. In the various exemplary embodiments shown in Fig. 2, Specimen Nos. 20 to 30 can be first subjected to a thermal treatment protocol of Specimen No. 7 as described above. Specimen Nos. 20 to 30 can then be subjected to various types of second ageing treatment, such as those illustrated in Fig. 2. For example, Specimen No. 21 can be subjected to a second ageing treatment at the temperature of about 300°C for about half an hour and then quenched by water. The resulting material can have an initial austenite phase starting temperature of about 25°C, an initial austenite phase peak temperature of about 33.5°C, and an initial austenite phase finish temperature of about 50°C.

In another exemplary embodiments shown in Fig. 3, Specimen Nos. 31 to 42 can be first subjected to a thermal treatment protocol of Specimen No. 14 as described above. Specimen Nos. 31 to 42 can then be subjected to various types of second ageing treatment, such as those illustrated in Fig. 3. For example, Specimen No. 38 can be subjected to a second ageing treatment at the temperature of about 300°C for about one hour and then quenched by water. The resulting material can have an initial austenite phase starting temperature of about 26°C, an initial austenite phase peak temperature of about 36.5°C, and an initial austenite phase finish temperature of about 44°C.

Fig. 4 shows the mechanical testing results of Specimen No. 5. The initial transition temperature A_f of this Specimen is 10°C above the human body temperature, while super-elasticity or pseudo-elasticity is seen at the human body temperature.

While various thermal treatment protocols have been illustrated to make a shape memory and/or super-elastic material and/or adjust the initial transition temperature A_f of the shape memory and/or super-elastic material to be above a body temperature, it will be appreciated that various other protocols for adjusting the initial transition temperature A_f are also within the scope of the present invention.

It will be appreciated that the various features described herein may be used singly or in any combination thereof. Therefore, the present invention is not limited to only the embodiments specifically described herein. While the foregoing description and drawings represent a preferred embodiment of the present invention, it will be understood that various additions, modifications, and substitutions may be made therein without departing from the spirit of the present invention. In particular, it will be clear to those skilled in the art that the present invention may be embodied in other specific forms, structures, arrangements, proportions, and with other elements, materials, and components, without departing from the spirit or essential characteristics thereof. One skilled in the art will appreciate that the invention may be used with many modifications of structure, arrangement, proportions, materials, and components and otherwise, used in the practice of the invention, which are particularly adapted to specific environments and operative requirements without departing from the principles of the present invention. The presently disclosed embodiments are therefore to be considered in all respects as illustrative and not restrictive.

CLAIMS

What is claimed is:

1. A shape memory material having an initial transition temperature A_f above a body temperature.

2. The shape memory material of claim 1, wherein the initial transition temperature A_f is about 0°C to about 15°C above a body temperature.

3. The shape memory material of claim 1, wherein the initial transition temperature A_f is about 10°C to about 15°C above a body temperature.

4. The shape memory material of claim 1 being malleable at a room temperature.

5. The shape memory material of claim 1 being super-elastic or pseudo-elastic at a body temperature.

6. The shape memory material of claim 1 comprising a nickel titanium alloy, in which nickel and titanium are in the ratio of about 50% to 50%.

7. An article being formed of the shape memory material of claim 1.

8. The article of claim 7 being an implant selected from the group consisting of a plate, a rod, a wire, a screw, and any combination thereof.

9. A method of making a shape memory material comprising:

providing a raw material in the form of a solid solution; and

treating the raw material to provide a shape memory material having an initial transition temperature A_f above a body temperature.

10. The method of claim 9, wherein the treatment is selected from the group consisting of thermo-treatment, thermo-mechanical treatment, radiation treatment, ternary alloying, and any combination thereof.

11. The method of claim 9 further comprising a mechanical treatment selected from the group consisting of compression, tensile, bending, torsion, cold working, hot working, and any combination thereof.

12. A shape memory material being formed according to claim 11.

13. An article being formed of the shape memory material of claim 12.

14. The article of claim 13 being super-elastic and providing a substantially constant force, wherein the force is determined by one or more factors selected from the group consisting of the size of the article, the number of the article, the composition of the shape memory material, the thermal treatment, the thermo-mechanical treatment, the radiation treatment, the ternary alloying, or any combinations of the above.

15. A method of making a shape memory and/or super-elastic material, comprising:

heating a raw material; and

subjecting the heat-treated raw material to an ageing treatment to form a shape memory and/or super-elastic material.

16. The method of claim 15, wherein the raw material is heated at a temperature ranging from about 700°C to about 900°C for a time period of about 0.5 to 2 hours.

17. The method of claim 15, wherein the raw material is heated at a temperature ranging from about 800°C to about 900°C.

18. The method of claim 15, wherein the treated raw material is subjected to an ageing treatment at a temperature ranging from about 200°C to about 520°C for a time period of about 0.25 to 2 hours.

19. The method of claim 15, wherein the ageing treatment is carried out at a temperature ranging from about 250°C to about 500°C.

20. The method of claim 15, wherein the ageing treatment is carried out for a time period of about 0.5 to 2 hours.

21. The method of claim 15, wherein the shape memory and/or super-elastic material has an initial austenite phase finishing temperature of about 0°C to about 15°C above a body temperature.

22. The method of claim 15, further comprising a second ageing treatment which is carried out at a temperature ranging from about 200°C to about 500°C for a time period of about 0.5 to 2 hours.

23. The method of claim 22, wherein the second ageing treatment is carried out at a temperature ranging from about 250°C to about 500°C.

24. The method of claim 22, wherein the second ageing treatment is carried out for a time period of about 0.5 to 1 hour.

25. A material being formed according to claim 15.

26. An article formed of the material of claim 25.

No. of Specimen	*Solid Solution Temperature (℃)*	*Time for Solid Solution (Hours)*	*Cooling Method*	*Ageing Temperature (℃)*	*Time for Ageing (Hours)*	*Cooling Method*	*Austenite Phase Starting Temp. (℃)*	*Austenite Phase Peak Temp. (℃)*	*Austenite Phase Finish Temp. (℃)*
1	800	1	Inside furnace	450	0.5	Water quench	26	33.5	47
2	800	1	Inside furnace	400	0.5	Water quench	26	29	52
3	800	1	Inside furnace	400	0.5	Inside furnace	37.5	41	58
4	800	1	Water quench	450	0.5	Water quench	26.5	33	58
5	800	1	Inside furnace	450	0.5	Water quench	26	33.5	47
6	800	1	Inside furnace	450	0.5	Inside furnace	30.5	36.5	48
7	800	1	Inside furnace	450	0.75	Water quench	16	22.5	44
8	800	1	Inside furnace	450	0.75	Inside furnace	35	39	56
9	800	1	Inside furnace	460	0.5	Inside furnace	35.5	39	47
10	800	1	Inside furnace	460	0.75	Inside furnace	34	36.5	60
11	800	1	Inside furnace	480	0.5	Inside furnace	29	33	55
12	800	1	Inside furnace	480	0.75	Inside furnace	29	35	54
13	800	1	Inside furnace	500	0.5	Water quench	30	36	50
14	800	1	Inside furnace	500	0.5	Inside furnace	12	32	43
15	800	1	Inside furnace	500	0.25	Inside furnace	27	34	45
16	800	1	Inside furnace	500	0.33	Inside furnace	29	34	45
17	800	1	Inside furnace	520	0.5	Inside furnace	10	28	42
18	850	1	Water quench	450	0.5	Water quench	31.5	34.5	72
19	900	1	Inside furnace	450	0.5	Inside furnace	27	34	57

Fig. 1

No. of Specimen	2^{nd} Ageing Temperature (℃)	Time for 2^{nd} Ageing (Min.)	Cooling Method	Austenite Phase Starting Temp. (℃)	Austenite Phase Peak Temp. (℃)	Austenite Phase Finish Temp. (℃)	Remarks
20	250	30	Water quench	15	22.5	40	Specimen Nos. 20 to 30 were subjected to solid solution treatment at 800°C for 1 hour and cooled down inside furnace. Then, these specimens were treated by ageing at 450°C for 0.75 hour and were then quenched by water.
21	300	30	Water quench	25	33.5	50	
22	300	40	Water quench	27	36	56	
23	300	60	Water quench	29	35.5	58	
24	350	30	Water quench	29.5	35	53	
25	350	40	Water quench	32	38.5	60	
26	350	60	Water quench	38.5	45	65	
27	400	30	Water quench	35	42	43	
28	400	40	Water quench	42.5	48.5	64	
29	400	60	Water quench	38.5	45	61	
30	250	30	Water quench	15	22.5	40	

Fig. 2

No. of Specimen	*2nd Ageing Temperature (℃)*	*Time for 2nd Ageing (Min.)*	*Cooling Method*	*Austenite Phase Starting Temp. (℃)*	*Austenite Phase Peak Temp. (℃)*	*Austenite Phase Finish Temp. (℃)*	*Remarks*
31	200	30	Inside furnace	22	33	43	Specimen Nos. 31 to 42 were subjected to solid solution treatment at 800°C for 1 hour and cooled down inside furnace. Then, these specimens were treated by ageing at 500°C for 0.5 hour and were then cooled inside furnace.
32	200	30	Water quench	21	30	40	
33	200	60	Inside furnace	13	27.5	40	
34	200	60	Water quench	27	35	47	
35	300	30	Inside furnace	7	28	50	
36	300	30	Water quench	18	29	41	
37	300	60	Inside furnace	15	31.5	44	
38	300	60	Water quench	26	36.5	44	
39	400	30	Inside furnace	31	44	60	
40	400	30	Water quench	26	38	52	
41	400	60	Inside furnace	35	49	64	
42	400	60	Water quench	27	42.5	56	

Fig. 3

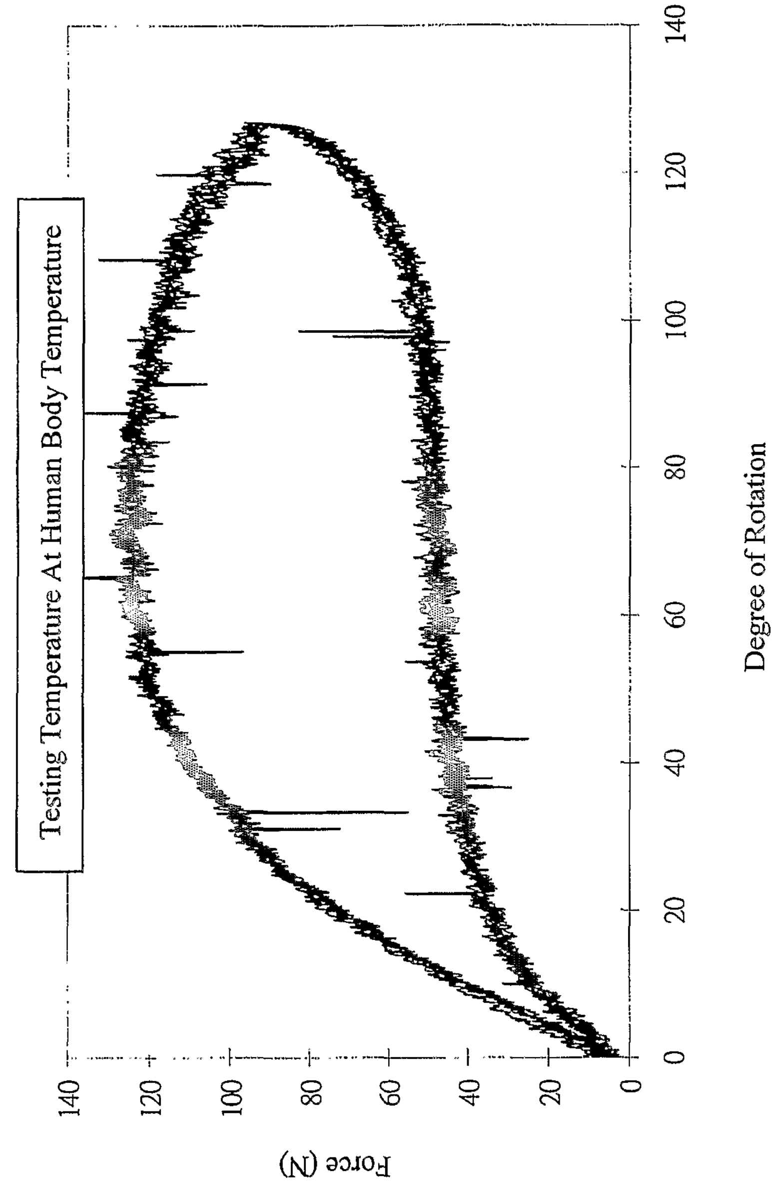
Testing Temperature At Human Body Temperature
Force (N)
0
20
40
60
80
100
120
140
Degree of Rotation
0
20
40
60
80
100
120
140

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2004/000371

A. CLASSIFICATION OF SUBJECT MATTER

IPC[7] C22C19/00 C22F1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC[7] C22C C22F A61B A61F A61L A61M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

CN-PAT

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, EPODOC, PAJ,CN-PAT, CNKI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN2055045U (BEIJING NONFERROUS METALS GEN INST) 28.Mar.1990 (28.03.1990) see description page 2, lines 3-5,claim 2 （Family: none）	1,2,7,8
X	CN 1119093A (TOKIN CORP) 27.Mar.1996 (27.03.1996) see description page3, lines 3-9	1,2,5,7
X	JP 2-41426A (FURUKAWA ELECTRIC CO LTD , MEMORY KK) 09.Feb.1990 (09.02.1990) （Family: none） see page 2, column 1, lines 5-16, page 3,column 1, lines 14-16	1—4,6,7
X	CN2152563Y (DONGNAN UNIVERSITY） 12.Jan.1994 (12.01.1994) （Family: none） see description page 1, lines 17-21, description page 2,lines 1-5	15,16,18—20,25,26
A	JP1-242763A （HITACHI METALS LTD） 27.Sept.1989 (27.09.1989) （Family: none） whole document	1—26

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9.July.2004	29 · JUL 2004 (2 9 · 0 7 · 2 0 0 4)

Name and mailing address of the ISA/CN	Authorized officer
6 Xitucheng Rd, Jimen Bridge, Haidian District, Beijing 100088, China	Pang Limin 敏庞 印立
Facsimile No. (86-10)62019451	Telephone No. (86-01)62084726

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2004/000371

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

A shape memory material having an Af temprature above a body temprature and method of making it.
A method of making a shape memory material.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant,this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant.Consequently ,this international search report is restricted to the invention first mentioned in the claims;it is covered by claims Nos.:

Remark on protest ☐ The acditional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2004/000371

CN1119093 A	27.03.1996	DE69527672E E	12.09.2002
		EP0679377 A2	02.11.1995
		JP8010278 A	16.01.1996
		EP0679377 A3	08.05.1996
		US5607756 A	04.03.1997
		KR251013 B1	01.06.2000
		EP0679377 B1	07.08.2002
CN2055045U	28.03.1990	None	
JP 2-41426A	09.02.1990	None	
CN2152563Y	12.01.1994	None	
JP 1-242763A	27.09.1989	None	