US 20080260573A1

(19) United States
(12) Patent Application Publication
Ishida et al.
(10) Pub. No.: US 2008/0260573 A1
(43) Pub. Date: Oct. 23, 2008

(54) TERNARY TI-NI-CU SHAPE MEMORY ALLOY AND PROCESS FOR PRODUCING SAME

(76) Inventors: **Akira Ishida**, Ibaraki (JP); **Morio Sato**, Ibaraki (JP)

Correspondence Address:
WENDEROTH, LIND & PONACK, L.L.P.
2033 K STREET N. W., SUITE 800
WASHINGTON, DC 20006-1021 (US)

(21) Appl. No.: 11/922,026

(22) PCT Filed: May 24, 2006

(86) PCT No.: PCT/JP2006/310344

§ 371 (c)(1), (2), (4) Date: Jan. 30, 2008

(30) Foreign Application Priority Data

Jun. 13, 2005 (JP) 2005-172939

Publication Classification

(51) Int. Cl.
C22C 30/02 (2006.01)

(52) U.S. Cl. 420/587

(57) ABSTRACT

An amorphous Ti—Ni—Cu alloy comprising from 44 to 49 atomic % of Ti, from 20 to 30 atomic % of Cu, and the balance being Ni and unavoidable elements is heated at **500** to 700° C. for a period of time not exceeding 100 hours to crystallize the amorphous alloy.

FIG. 1

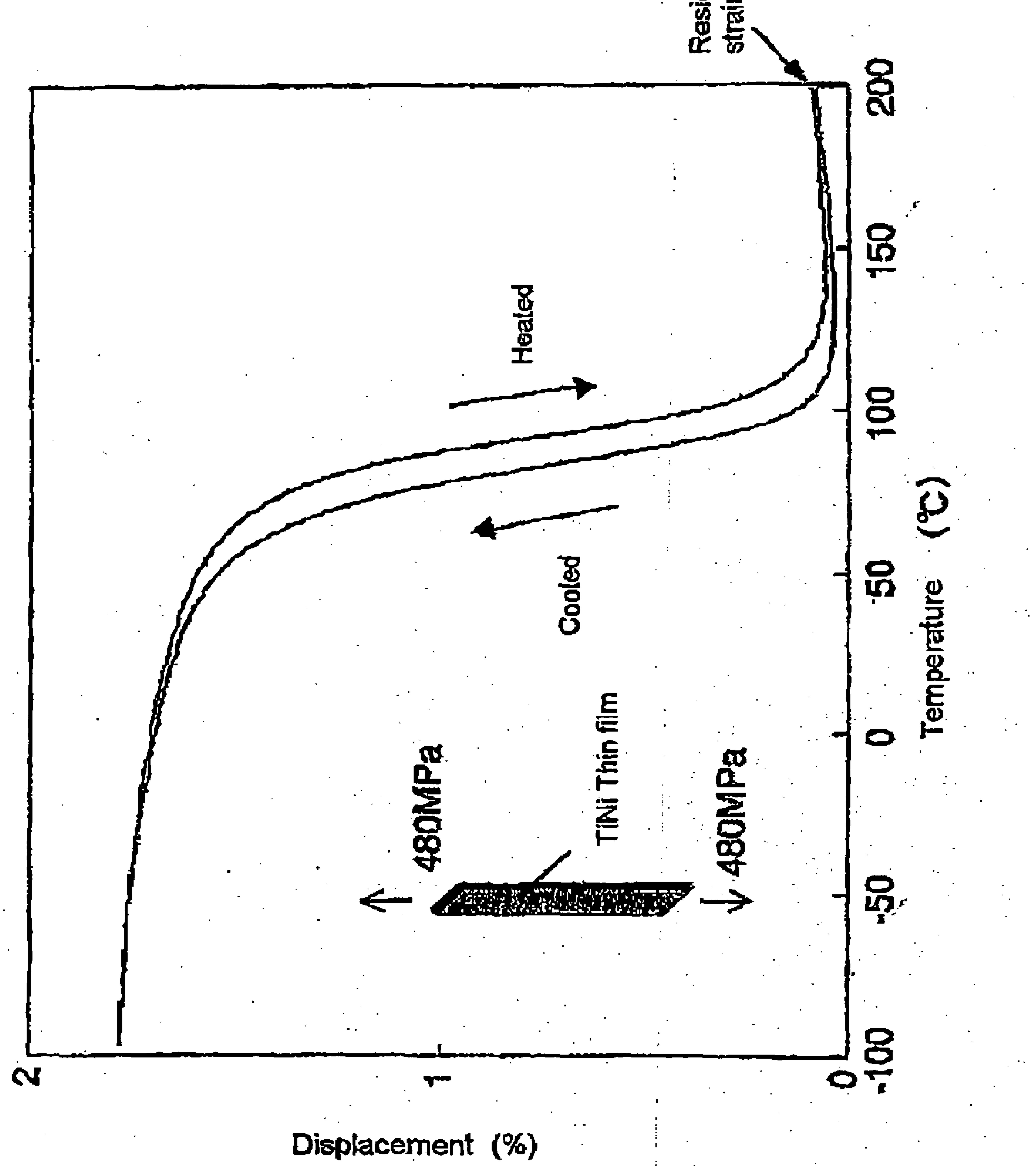

Residual strain
Heated
Cooled
480MPa
TiNi Thin film
480MPa
Displacement (%)
0
1
2
Temperature (°C)
-100
-50
0
50
100
150
200

FIG. 2

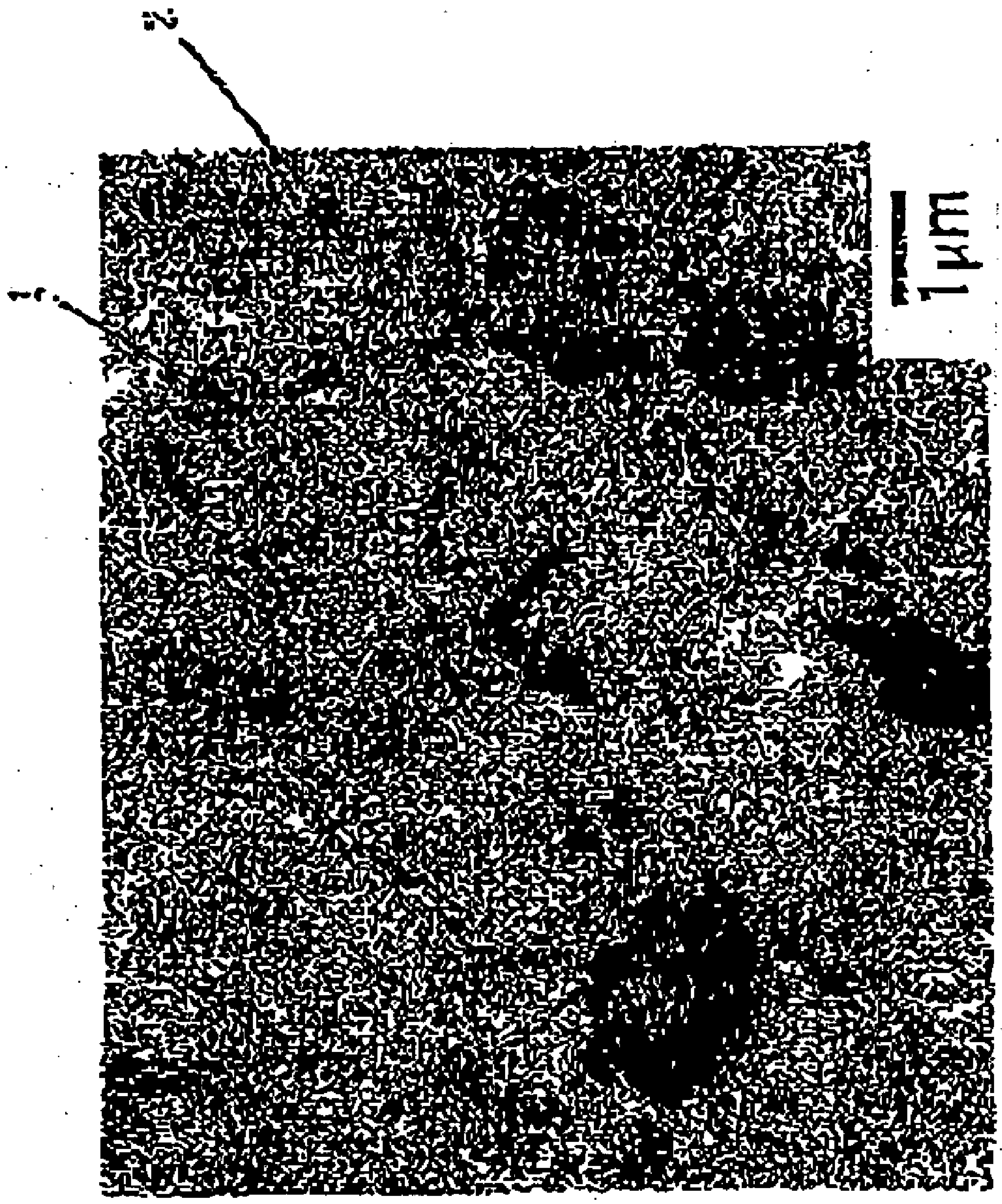


FIG. 3

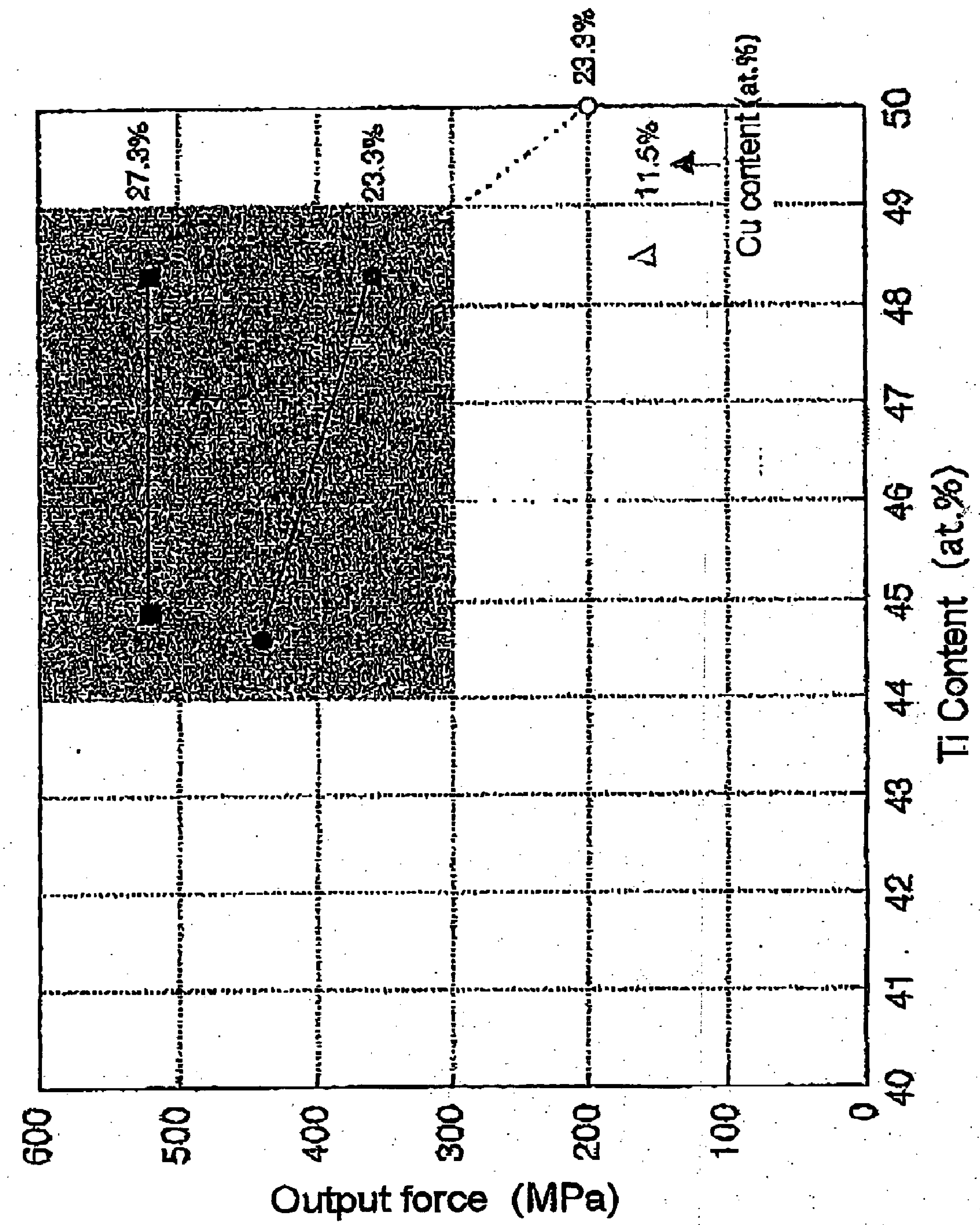

27.3%
23.3%
23.9%
11.5%
Cu content (at.%)
Output force (MPa)
Ti Content (at.%)
600
500
400
300
200
100
0
40
41
42
43
44
45
46
47
48
49
50

FIG. 4

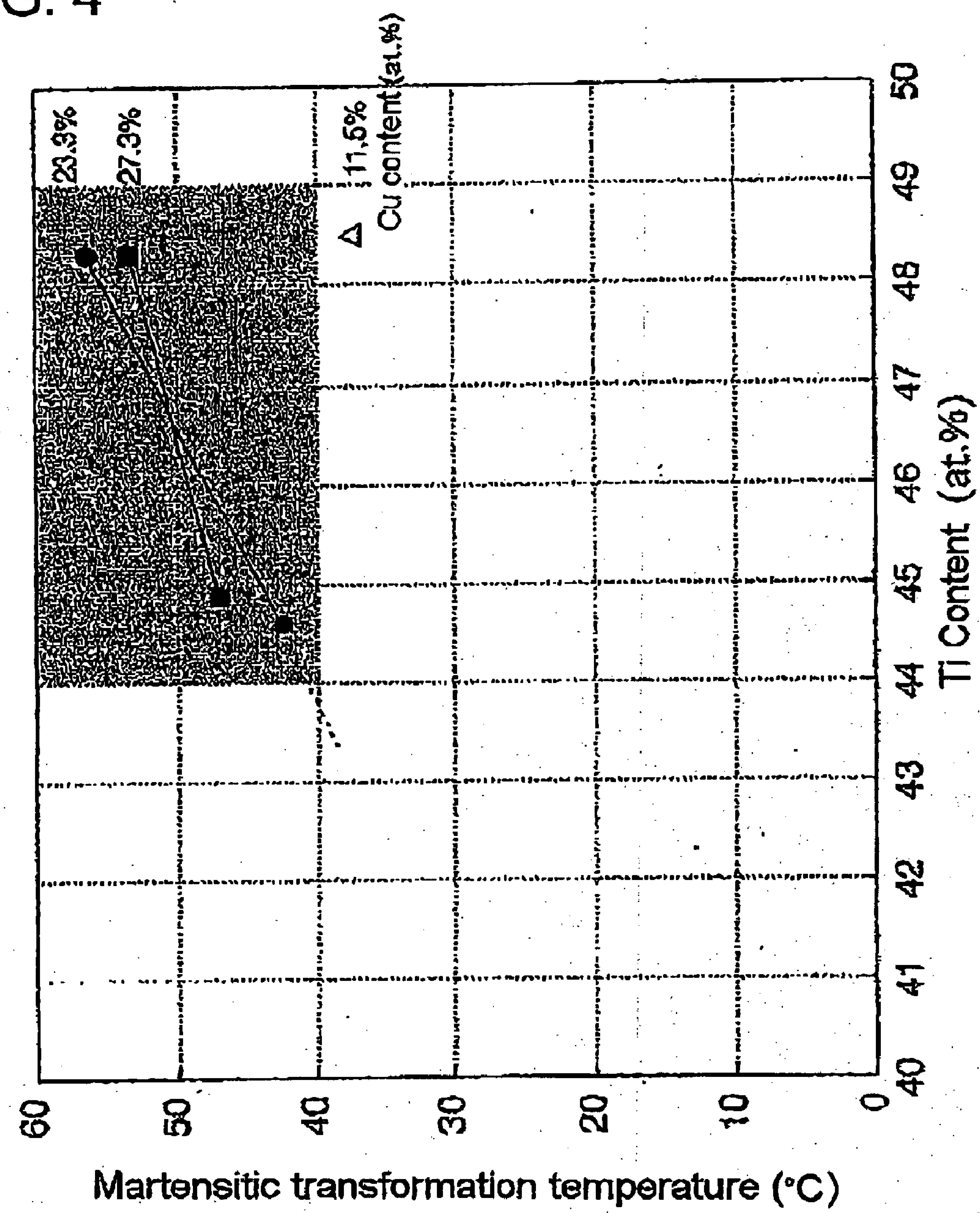

23.3%
27.3%
Δ 11.5%
Cu content (at.%)
Ti Content (at.%)
40
41
42
43
44
45
46
47
48
49
50
Martensitic transformation temperature (°C)
60
50
40
30
20
10
0

FIG. 5

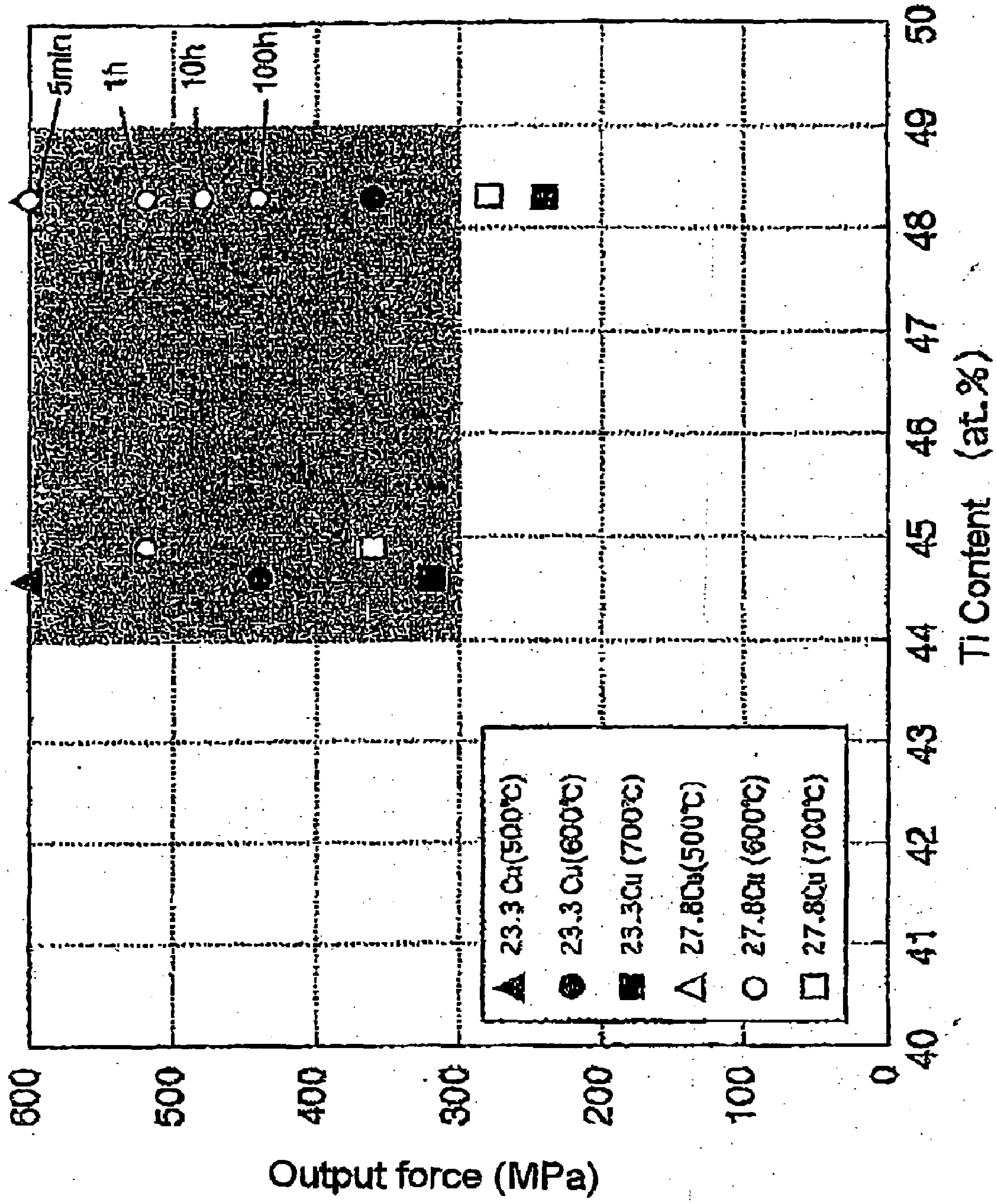
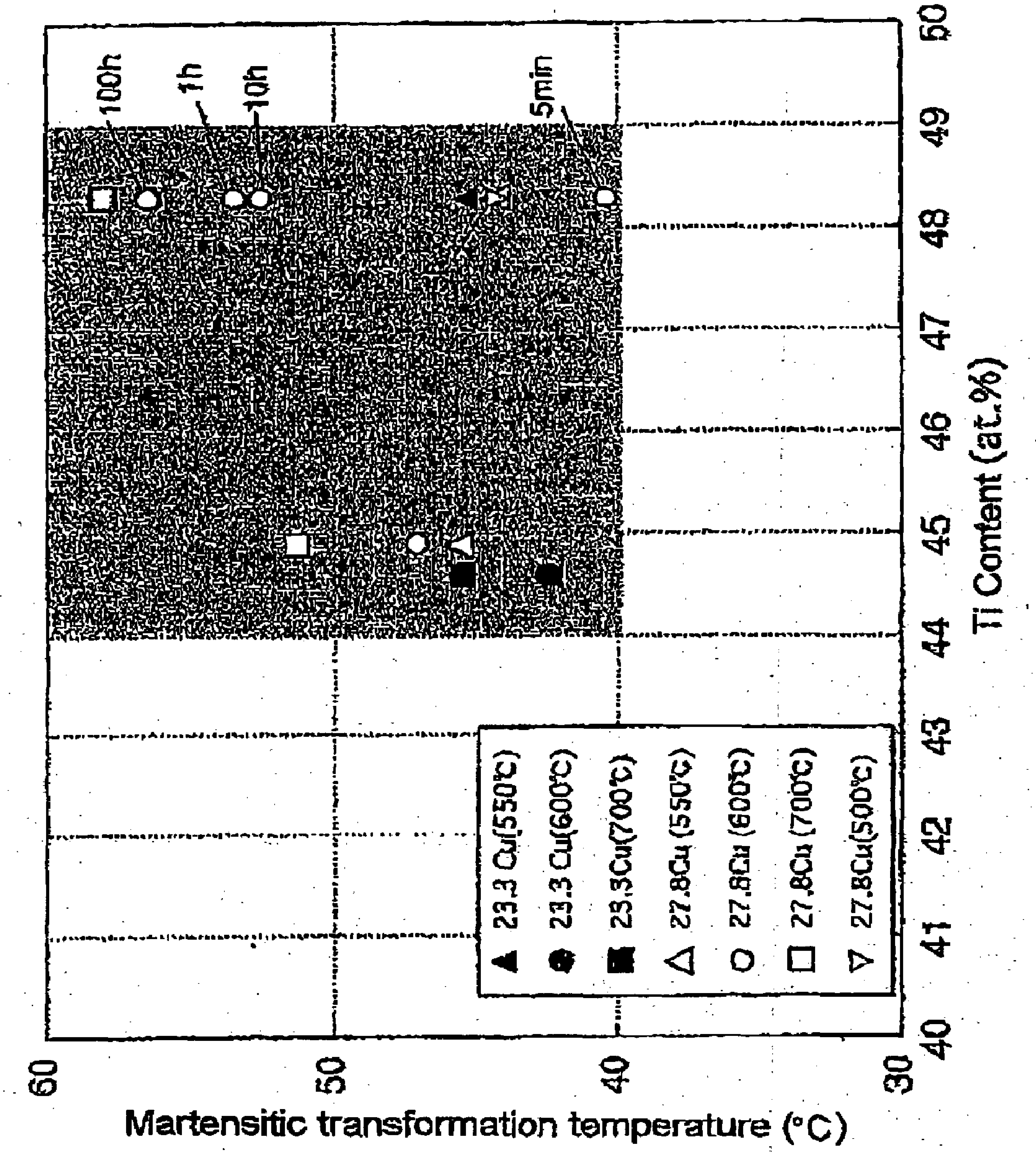
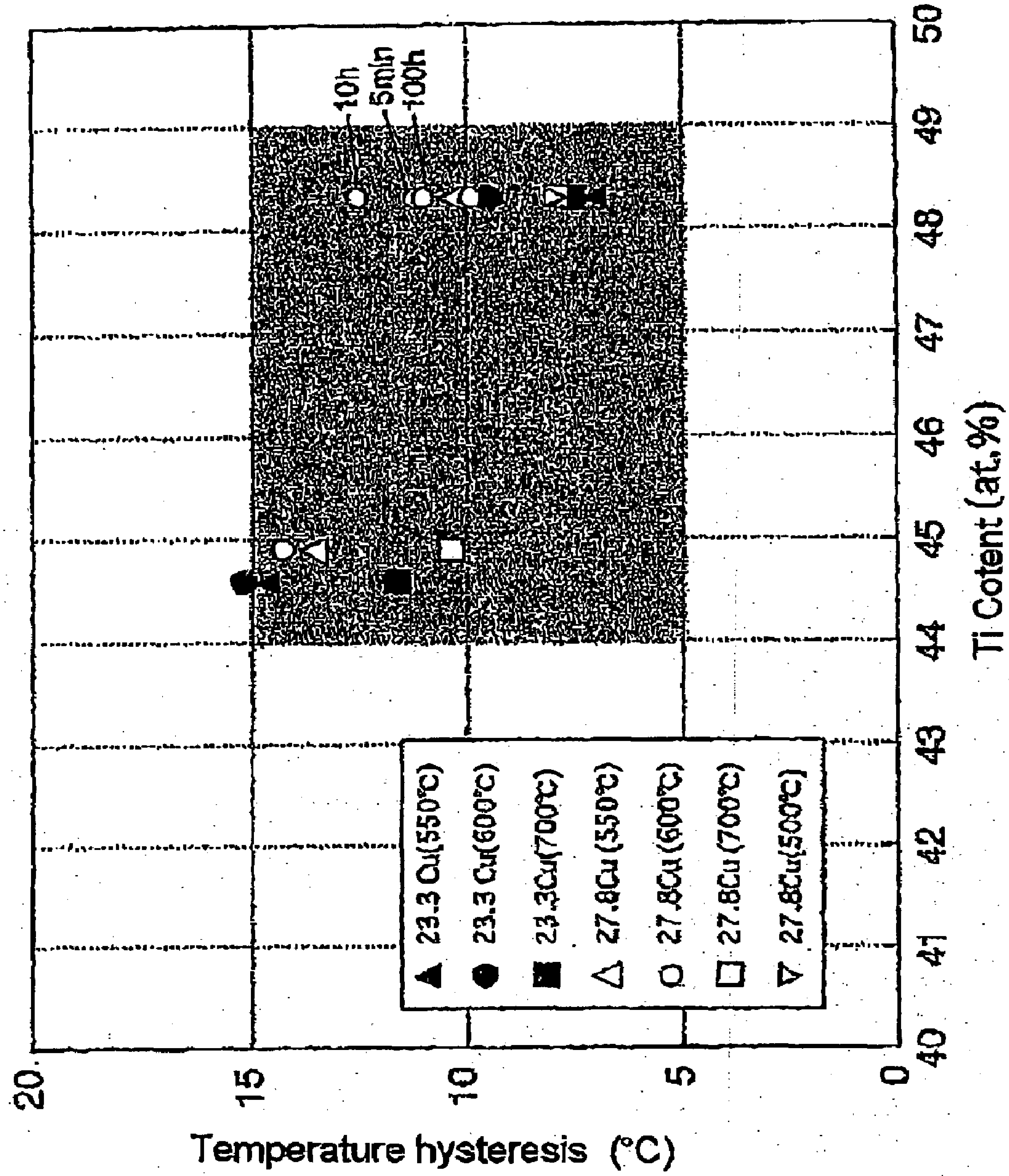

5min
1h
10h
100h
23.3 Cu(500°C)
23.3 Cu(600°C)
23.3Cu (700°C)
27.8Cu(500°C)
27.8Cu (600°C)
27.8Cu (700°C)
600
500
400
300
200
100
0
Output force (MPa)
40
41
42
43
44
45
46
47
48
49
50
Ti Content (at.%)

FIG. 6



Martensitic transformation temperature (°C)
Ti Content (at.%)
100h
1h
10h
5min
23.3 Cu(550°C)
23.3 Cu(600°C)
23.3Cu(700°C)
27.8Cu (550°C)
27.8Cu (600°C)
27.8Cu (700°C)
27.8Cu(500°C)
60
50
40
30
40
41
42
43
44
45
46
47
48
49
50

FIG. 7


Temperature hysteresis (°C)
Ti Cotent (at.%)
20
15
10
5
0
40
41
42
43
44
45
46
47
48
49
50
10h
5min
100h
23.3 Cu(550°C)
23.3 Cu(600°C)
23.3Cu(700°C)
27.8Cu (550°C)
27.8Cu (600°C)
27.8Cu (700°C)
27.8Cu(500°C)

TERNARY TI-NI-CU SHAPE MEMORY ALLOY AND PROCESS FOR PRODUCING SAME

TECHNICAL FIELD

[0001] The present invention relates to a ternary Ti—Ni—Cu shape memory alloy which has both low composition dependency and low heat treatment dependency and which is useful as a device used, for example, in an actuator, and to a process for producing same.

BACKGROUND ART

[0002] A binary Ti—Ni alloy which is widely used as a shape memory alloy has defects because its phase transformation temperature greatly depends upon its composition and its heat treatment temperature and is lower than ambient temperature when a large output force is attempted to be obtained. Thus, a difficulty is encountered in controlling the composition. In particular, the yield of sputtered thin films in which the compositional distribution in the plane direction unavoidably becomes non-uniform is poor. It is, therefore, difficult to produce sputtered films on an industrial scale (Patent Document 1).

[0003] With a view toward solving the above problems of such a binary Ti—Ni alloy, studies have been made on a ternary Ti—Ni—Cu shape memory alloy in which a part of Ni of a 50 atomic % Ti—Ni alloy is substituted with Cu. For example, it has been revealed that in Ti—Ni—Cu alloy thin films having a Ti content of at least 50 atomic %, the temperature hysteresis is reduced by addition of Cu and the recovery stress increases due to solid solution hardening by Cu (Non-Patent Document 1). It has been also revealed that in Ti—Ni—Cu alloy thin films containing 6 atomic % of Cu and no more than 50 atomic % of Ti, the shape memory behavior of alloys having a structure in which a TiNiCu phase is formed within grains greatly varies with a Ti content and, further, the transformation occurs in a temperature range lower than ambient temperature and in two separate stages (Non-Patent Document 2).

[0004] A Ti50-(Ni, Cu)50 alloy which is a ternary Ti—Ni—Cu shape memory alloy, however, is brittle and has poor workability, though its phase transformation temperature scarcely depends upon the Cu content. Thus, the Cu content is at most 10 atomic % in the case of a cast alloy and is at most 20 atomic % in the case of an alloy formed by a liquid quenching method. Additionally, the obtained alloy has a composition near the Ti(Ni, Cu) single phase (Ti 50 atomic %) and is defective in that the output force is small. For example, there is proposed a method of producing a Ti—Ni—Cu alloy which contains more than 10 atomic % of Cu and which is difficult to be produced with the ordinary melting and hot processing method (Patent Document 2). Since the composition of the produced alloy is limited to the single phase region in the vicinity of Ti-50 atomic %, however, the alloy has a defect that the output force is small.

[0005] Patent Document 1: JP-B-2899682

[0006] Patent Document 2: JP-A-H06-172886

Non-Patent Document 1

[0007] [Transformation and Deformation Behavior in Sputter-Deposited Ti—Ni—Cu Thin Films], T. Hashinaga, S. Miyazaid, T. Ueki and H. Hirokawa: J. Physique IV, 5(1995), C8-689

Non-Patent Document 2

[0008] "Structure Evolution in Sputtered Thin Films of Tix (Ni, Cu)1−x" [1: Diffusive transformations], [2: Displace Transformations], L. Chang and D. S. Grumman: Philosophical Magazine A 76(1997), 163-219

DISCLOSURE OF INVENTION

Problems to be Solved by the Invention

[0009] As described in the foregoing, since the conventional shape memory alloy thin film are sensitive to composition variations and heat treatment conditions, it has been difficult to properly control their composition and heat treatment conditions. Further, with the customarily employed sputtering method, it has not been easy to obtain a uniform distribution of the alloy composition in the plane direction thereof and to produce such films in a satisfactory yield. It has been, therefore, difficult to produce shape memory alloy thin films on an industrial scale. Further, since various treatments for increasing the output force of a shape memory alloy tend to lower the transformation temperature and ductility of the alloy, it has been difficult to produce a shape memory alloy which has a high transformation temperature and a large output force and, yet which has useful ductility.

[0010] In this circumstance, the objective of the present invention is to provide a ternary Ti—Ni—Cu shape memory alloy which has solved the above-described problems, which has low composition dependency, which permits stable production, which has a transformation temperature higher than ambient temperature and which can generate a large output force, and to provide a process capable of producing such a ternary Ti—Ni—Cu shape memory alloy in an efficient manner.

Means for Solving the Problems

[0011] In accomplishing the foregoing objects, there is provided in accordance with a first aspect of the present invention a ternary Ti—Ni—Cu shape memory alloy comprising from 44 to 49 atomic % of Ti, from 20 to 30 atomic % of Cu, and the balance being Ni and unavoidable elements.

[0012] In a second aspect, the present invention provides the above alloy, wherein a TiNiCu or TiCu phase of not greater than 500 nm is formed within Ti(Ni, Cu) crystal grains having a grain size of 2 μm or less.

[0013] In a third aspect, the present invention provides a process, which comprises beating an amorphous Ti—Ni—Cu alloy comprising from 44 to 49 atomic % of Ti, from 20 to 30 atomic % of Cu, and the balance being Ni and unavoidable elements to crystallize the amorphous Ti—Ni—Cu alloy.

[0014] In a fourth aspect, the present invention provides the above process, wherein said heating is at a temperature in the range of from 500 to 700° C.

[0015] In a fifth aspect, the present invention provides the above process, wherein said heating is performed for a period of time not exceeding 100 hours.

Effect of the Invention

[0016] The ternary Ti—Ni—Cu shape memory alloy according to the present invention has low composition or heat treatment dependency and a transformation temperature higher than ambient temperature and is capable of being produced in a stable manner. The shape memory alloy is useful as a device used, for example, in an actuator.

[0017] The present invention also provides a process capable of producing the above ternary Ti—Ni—Cu shape memory alloy in an efficient manner.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] FIG. **1** shows shape memory characteristics of a 48.3 Ti-27.8 Cu—Ni alloy obtained by heat treatment at 600° C. for 1 hour.

[0019] FIG. **2** is a microphotograph showing the structure of a 48.3 Ti-27.8 Cu—Ni alloy obtained by heat treatment at 600° C. for 1 hour.

[0020] FIG. **3** shows Ti content dependence and Cu content dependence of the output force generated by a Ti—Ni—Cu alloy obtained by heat treatment at 600° C. for 1 hour.

[0021] FIG. **4** shows Ti content dependence and Cu content dependence of the martens tic transformation temperature of a Ti—Ni—Cu alloy obtained by beat treatment at 600° C. for 1 hour.

[0022] FIG. **5** shows heat treatment temperature dependence (for a heat treatment time of 1 hour) and heat treatment time dependence (for a heat treatment temperature of 600° C.) of the output force generated by Ti—Ni—Cu alloys of various compositions.

[0023] FIG. **6** shows heat treatment temperature dependence (for a heat treatment time of 1 hour) and heat treatment time dependence (for a heat treatment temperature of 600° C.) of the martensitic transformation temperature of Ti—Ni—Cu alloys of various compositions.

[0024] FIG. **7** shows heat treatment temperature dependence (for a heat treatment time of 1 hour) and heat treatment time dependence (for a heat treatment temperature of 600° C.) of the temperature hysteresis of Ti—Ni—Cu alloys of various compositions.

DESCRIPTION OF REFERENCE NUMERALS

[0025] **1**: grain boundary precipitates

[0026] **2**: precipitates within grains

BEST MODE FOR CARRYING OUT THE INVENTION

[0027] In the studies on ternary Ti—Ni—Cu alloys of B 19 structure in which the change in crystal structure is small, it has been found that a ternary Ti—N—Cu shape memory alloy exhibiting, in a stable maimer without being influenced by the alloy composition or heat treatment conditions, transformation at a temperature higher than ambient temperature and capable of generating a large output force can be obtained by adopting, in combination, enrichment of precipitates and solid solution hardening-in addition to microsize of grains (suppressing the grain size up to about 2 μm) which alone would cause lowering of the transformation temperature. The present invention has been completed based on the technical finding.

[0028] A large output force generated by the ternary Ti—Ni—Cu shape memory alloy according to the present invention is considered to be ascribed to the synergetic effect among the solid solution hardening by Cu atom, the precipitation of a TiNiCu phase or a TiCu phase within the Ti(Ni, Cu) crystal grains, and the microsize of the Ti(Ni, Cu) crystal grains. When the heat treatment is carried out at a high temperature for an excessively long period of time, however, the size of the crystal grains increases and the formation of such precipitates within the crystal grains decreases and, therefore, a high output force could not be obtained. For this reason, the heat treatment is preferably carried out at 500 to 700° C. for 100 hours or less.

[0029] In the process for producing a ternary Ti—Ni—Cu shape memory alloy according to the present invention, an amorphous Ti—Ni—Cu alloy composed of Ti in an amount of from 44 to 49 atomic %, Cu in an amount of from 20 to 30 atomic %, and the balance being Ni and unavoidable elements is heated at a temperature from 500 to 700° C. for a period of time not exceeding 100 hours. The reasons for specifying the contents of the above elements are as follows. When the Ti content exceeds 49 atomic %, a TiNiCu phase which is one of the factors to increase the output force of the ternary Ti—Ni—Cu shape memory alloy is not formed. When the Ti content is less than 44 atomic %, on the other hand, the TiNiCu phase increases excessively to cause not only lowering of the transformation temperature but also brittleness of the alloy. Therefore, the Ti content should be within the range of from 44 to 49 atomic %. When the Cu content exceeds 30 atomic %, only a TiCu phase is formed and the alloy becomes brittle. On the other hand, when the Cu content is less than 20 atomic %, the transformation temperature is lowered so that it is no longer possible to ensure a transformation temperature higher than ambient temperature (suitably 40° C. or higher) in a stable manner throughout the entire range of 49 to 44 atomic % of the Ti content. Further, a large output force cannot be obtained because the solid solution hardening by Cu is insufficient and the grain size becomes large. Therefore, the Cu content should be within the range of from 20 to 30 atomic %. The following example will further specifically illustrate the ternary Ti—Ni—Cu shape memory alloy and its production process.

EXAMPLE

[0030] Amorphous alloy thin films of 48.3 atomic % Ti-23.3 atomic % Cu—Ni; 48.3 atomic % Ti-27.8 atomic % Cu—Ni; 44.6 atomic % Ti-23.2 atomic % Cu—Ni; and 44.9 atomic % Ti-27.3 atomic % Cu—Ni were produced using a multi-target magnetron sputtering system. Such amorphous thin films may be produced not only by sputtering but also by using any other suitable method. Each of the amorphous thin films was peeled off from a substrate and subjected to a heat treatment at 500 to 700° C. The obtained alloy films were measured for their transformation temperature by differential thermal analysis and for their shape memory characteristics by heating and cooling under a loaded state.

[0031] FIG. **1** shows an example of the measured results of shape memory characteristics, from which it is seen that almost no residual strain remains upon cooling and heating under a high load stress and that the transformation temperature is higher than ambient temperature.

[0032] FIG. **2** is an electron microphotograph showing the structure of one of the obtained ternary Ti—Cu—Ni shape memory alloys. Thermally stable, micro-size (500 nm or less) TiCu phase 1 or TiNiCu phase 2 is formed within the crystal grains or in the grain boundaries. The crystal grain size is limited to not greater than 2 μm. As a result of synergism among the promotion of microsize crystal grains, the enrichment of precipitates within grains and the solid solution hardening by Cu, it is possible to improve brittleness common to cast alloys and, at the same time, to obtain a high resistance to plastic deformation which would cause residual strains.

[0033] FIG. **3** shows composition dependence of the output force generated by one of the obtained ternary Ti—Cu—Ni shape memory alloys. The output force is represented by the stress causing a residual strain of at least 0.03%. It is seen that when the Cu content is 20 atomic % or higher, a high output force is obtained in a stable manner throughout the composition range of 49 to 44 atomic % Ti. It is also seen that, because of the formation of precipitates, the 48.3 atomic % Ti-23.3 atomic % Cu—Ni alloy shows a higher output force as compared with 50 atomic % Ti-23.3 atomic % Cu—Ni alloy and that, because of the solid solution hardening by Cu, the 48.3 atomic % Ti-23.3 atomic % Cu—Ni alloy shows a higher output force as compared with 48.3 atomic % Ti-11.5 atomic % Cu—Ni alloy. A TiNiCu phase and a TiCu phase precipitated in large amounts when the Ti content was less than 44 atomic % and when the Cu content exceeded 30 atomic %, respectively. Therefore, in either case, good shape memory alloys were not obtainable due to breakage.

[0034] FIG. **4** shows composition dependence of the transformation temperature (peak temperature). While ordinary shape memory alloys will cause a reduction of the transformation temperature if the composition is altered to obtain a high output force, a transformation temperature higher than ambient temperature is found to be obtained throughout the composition range of 49 to 45 atomic % Ti when the Cu content is in the range of 20 to 30 atomic %.

[0035] It has been confirmed that any of the above-described thin films of the ternary Ti—Ni—Cu shape memory alloy forms a low temperature phase (B19 phase) in the unloaded state at ambient temperature. FIG. **5** shows heat treatment dependence of the output force generated. It is appreciated that a high output force is obtainable in a wide range of heat treatment conditions.

[0036] However, the output force tends to lower when heat treatment time is prolonged and the heat treatment temperature is increased. The heat treatment at 500 to 700° C. for 100 hours or less is found to be preferred.

[0037] FIG. **6** shows beat treatment dependence of the martensitic transformation temperature. All of the alloys had a martensitic transformation temperature higher than ambient temperature. FIG. **7** shows the temperature hysteresis of the ternary Ti—Ni—Cu alloys. The temperature hysteresis of the transformation of any of the alloys is as small as 7 to 15° C.

1-5. (canceled)

6. A Ti—Ni—Cu shape memory alloy, containing Ti in amount of 44 atomic % to 49 atomic %, Cu in amount of 20 atomic % to 30 atomic % and the rest consisting of Ni and inevitable impurities, wherein TiNiCu phases or TiCu phases sized 500 nm or less precipitate in a Ti(Ni,Cu) crystal grain whose grain size is 2 μm or less.

7. A method of producing a Ti—Ni—Cu shape memory alloy, wherein an amorphous Ti—Ni—Cu alloy, which contains Ti in amount of 44 atomic % to 49 atomic %, Cu in amount of 20 atomic % to 30 atomic % and the rest consisting of Ni and inevitable impurities, is crystallized by heat treatment.

8. The method of producing a Ti—Ni—Cu shape memory alloy as claimed in claim **7**, wherein a temperature range of the heat treatment is 500° C. to 700° C.

9. The method of producing a Ti—Ni—Cu shape memory alloy as claimed in claim **7**, wherein time of the heat treatment is not beyond 100 hours.

10. The method of producing a Ti—Ni—Cu shape memory alloy as claimed in claim **8**, wherein time of the heat treatment is not beyond 100 hours.

* * * * *