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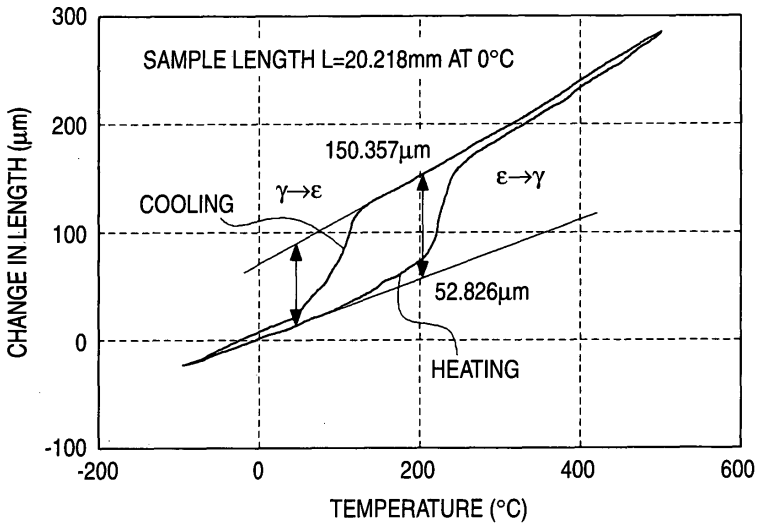
(54) Two-way shape-recovery alloy

(57) The present invention provides a two-way shape-recovery alloy, which contains less than 0.20 mass% of C, 13.00 to 30.00 mass% of Mn, 0.10 to 6.00 mass% of Si, 0.05 to 12.00 mass% of Cr, 0.01 to 3.00 mass% of Ni, and less than 0.100 mass% ofN, with the remainder being Fe and unavoidable impurities, in which the contents of Mn, Si, Cr and Ni satisfy the following expression (1):

$$600 \leq 33\mathrm{Mn} + 11\mathrm{Si} + 28\mathrm{Cr} + 17\mathrm{Ni} \leq 1050 \qquad (1).$$

FIG. 2



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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a two-way shape-recovery alloy. More particularly, the invention relates to a two-way shape-recovery alloy which can be caused to reversibly take a low-temperature-state shape and a high-temperature-state shape by utilizing the expansion and contraction which are accompanied phase transformations, without substantially utilizing a plastic deformation.

BACKGROUND OF THE INVENTION

[0002] When some kind of material is plastically deformed at a low temperature and thereafter heated to a high temperature, then the material returns to the shape which the material possessed before the plastic deformation. This phenomenon is referred to as shape-memory effect. Alloys showing the shape-memory effect are called shape-memory alloys.
Shape-memory alloys are expected to be used in applications such as

(1) a coil expander for changing the tension of a piston ring according to temperature (see International Publication WO 2004/090318),
(2) a system for controlling oil flow rate according to temperature (see JP-A-11-264425), and
(3) actuators and various switch parts which function also as a temperature sensor.

[0003] Various materials have conventionally been known as shape-memory alloys. Of these, Ti-Ni alloys are one of the most well known classes of shape-memory alloys. The Ti-Ni alloys which have undergone a shape-memory treatment at a high temperature are used in various applications. The shape-memory effect of Ti-Ni alloys is attributable to the following property: when a low-temperature phase (martensite phase) which has undergone a twin deformation with external force reversely transforms to a high-temperature phase (austenite phase), this system returns to the shape formed by a shape-memory treatment.
However, the Ti-Ni alloys have a problem that it is difficult to use the alloys in a wide range of applications because the material cost is high. There also is a problem that the alloys have a transformation temperature around room temperature and, hence, are not usable in applications where a shape-recovery temperature of 100°C or higher is required.
[0004] In contrast, iron-based shape-memory alloys represented by Fe-Mn-Si alloys are characterized by being inexpensive and having a high shape-recovery temperature. The shape-memory effect of iron-based alloys is attributable to the following property: when the ε phase generated by a stress-induced epsilon martensite transformation (transformation from the γ (FCC) phase to ε (HCP) phase induced by plastically deforming the system at a temperature not lower than M_s point and not higher than M_d point) reversely transforms to the γ phase, this system returns to the shape of the unprocessed system.
However, the iron-based shape-memory alloys have the following and other problems:

(1) the iron-based alloys are inferior in shape-memory effect to the Ti-Ni shape-memory alloys;
(2) the iron-based alloys are poor in corrosion resistance and oxidation resistance because they contain iron; and
(3) the iron-based alloys are apt to crack when plastically deformed in an annealed state.

[0005] In order to overcome those problems, various proposals have been made hitherto.
For example, JP-T-2000-501778 (the term "JP-T" as used herein means a published Japanese translation of a PCT patent application) discloses a nitrogen-containing iron-based shape-memory alloy which contains 28.80% of Mn, 5.24% of Si, 0.20% of Cr, and 0.11% of N, with the remainder of Fe.
This document includes a statement to the effect that not only the shape-memory characteristics but also mechanical properties, including damping characteristics, of an Fe-Mn alloy are improved by alloying with nitrogen.
[0006] JP-A-10-36943 discloses a process for producing an Fe-Mn-Si shape-memory alloy. In this process, an Fe-Mn-Si alloy having a given composition is shaped and then held for 15 minutes or more at a temperature higher than 1,000°C and lower than 1,200°C.
This document includes a statement to the effect that the process is effective in inhibiting the cracking which occurs upon stress deformation due to the intergranular precipitation of a fine intermetallic compound rich in manganese and silicon.
[0007] JP-A-2-221321 discloses a process for producing an iron-based shape-memory alloy. In this process, an Fe-Mn-Si alloy having a given composition is processed at a temperature not lower than the M_d' point (the temperature at which neither ε martensite nor α'martensite is induced by processing) and not higher than 700°C, and is then annealed

at a temperature not lower than (M_d' point + 200°C).
This document includes statements to the effect that:

(1) because the alloy is processed at a temperature not lower than the M_d' point, the generation of ε martensite and α' martensite, which adversely influence processability, can be inhibited and, hence, a processing limit can be greatly improved, and

(2) because annealing is conducted at a temperature not lower than (M_d' point + 200°C), the strain generated in the γ phase by the processing is eliminated or the γ phase recrystallizes, resulting in an improvement in shape-memory characteristics.

[0008] Furthermore, JP-A-7-292448 discloses an Fe-Mn-Si shape-memory alloy produced by subjecting an Fe-Mn-Si alloy having a given composition to a heat treatment to form the α phase having a thickness of 10 μm or larger in the surface thereof.
This document includes statements to the effect that:

(1) by subjecting the Fe-Mn-Si alloy to a heat treatment in a proper atmosphere, the α phase of the body-centered cubic structure having a lower manganese concentration than the matrix phase (γ phase) is formed in the surface, and
(2) since the α phase has higher corrosion resistance than the γ phase and has satisfactory conformability with the γ phase, flaking or cracking is less apt to occur even when the matrix phase deforms, whereby sufficient corrosion resistance is obtained.

[0009] In general, when a shape-memory alloy is plastically deformed at a temperature not higher than a transformation temperature and thereafter heated to a temperature not lower than the transformation temperature, then the shape thereof returns to the state of the alloy which has not undergone the plastic deformation. However, even when this alloy is cooled again to a temperature not higher than the transformation temperature, this alloy does not usually return to the shape imparted by the low-temperature plastic deformation. This phenomenon, in which only the shape of a high-temperature phase is memorized, is especially called "one-way shape-memory effect".
On the other hand, when some kind of shape-memory alloy is severely processed in the martensite state or is deformed in the martensite state and then subjected to constraint heating, then part of the low-temperature-phase shape can also be memorized. This phenomenon, in which both a shape of a high-temperature phase and a shape of a low-temperature phase are memorized, is especially called "two-way shape-memory effect". For example, it is known that a Ti-Ni alloy in which a texture has been partly formed shows the two-way shape-memory effect.
[0010] In the various applications shown above, such as coil expanders, oil flow rate control systems, and actuators, the shape-memory alloys are frequently required to have two-way working properties. Therefore, in order to apply a shape-memory alloy having a one-way shape-memory effect to a device required to have two-way working properties, it is necessary to combine this shape-memory alloy with another part to impart two-way working properties to the resultant device. Known methods for imparting two-way working properties include a method in which a one-way shape-memory alloy is combined with a spring, weight, or the like to impart two-way working properties (bias method) and a method in which two or more shape-memory parts are used (differential method).
However, such methods in which a one-way shape-memory alloy is combined with another part to impart two-way working properties have limitations in device miniaturization. Those methods are hence applicable to limited fields.
[0011] On the other hand, all the two-way shape-memory alloys which have been known are expensive and are poor in reproducibility. Only a limited number of such alloys have hence been put to practical use. The conventional iron-based shape-memory alloys show the property of returning from a shape formed by plastic processing to the shape which was possessed before the plastic processing, through a reverse transformation (ε→γ) (i.e., one-way shape-memory effect). However, the iron-based shape-memory alloys do not show a two-way shape-memory effect.
Furthermore, in order for a shape-memory alloy to be used in various applications, the alloy is required to have high accuracy of shape recovery and strength which enables the alloy to withstand repetitions of shape recovery.
However, no proposal has been made on an alloy which is inexpensive, has two-way working properties, has a higher shape-recovery temperature than Ti-Ni alloys (specifically, 90-100°C or higher), has high accuracy of shape recovery, and has strength which enables the alloy to withstand repetitions of shape recovery.

SUMMARY OF THE INVENTION

[0012] An object of the invention is to provide a two-way shape-recovery alloy which is inexpensive, has two-way working properties, has a higher shape-recovery temperature than Ti-Ni alloys, has high accuracy of shape recovery, and has strength which enables the alloy to withstand repetitions of shape recovery.

[0013] Namely, the present invention relates to the following items 1 to 4.

1. A two-way shape-recovery alloy, which comprises:

less than 0.20 mass% of C,
13.00 to 30.00 mass% of Mn,
0.10 to 6.00 mass% of Si,
0.05 to 12.00 mass% of Cr,
0.01 to 3.00 mass% ofNi, and
less than 0.100 mass% ofN,
with the remainder being Fe and unavoidable impurities,
wherein the contents of Mn, Si, Cr and Ni satisfy the following expression (1):

$$600 \leq 33Mn + 11Si + 28Cr + 17Ni \leq 1050 \qquad (1).$$

2. The two-way shape-recovery alloy according to item 1,
wherein the difference (A_f- M_s) between a transformation finish temperature in heating (A_f point) and a transformation start temperature in cooling (M_s point) is 150°C or smaller, and
wherein the alloy has a transformation start temperature in heating (A_s point) of 100°C or higher.
3. The two-way shape-recovery alloy according to item 1 or 2, which further comprises at least one of:

0.10 to 2.00 mass% of Mo,
0.10 to 2.00 mass% of W,
0.05 to 1.00 mass% of V, and
0.10 to 5.00 mass% of Co.

4. The two-way shape-recovery alloy according to any one of items 1 to 3, which further comprises
0.10 to 1.00 mass% of Cu+Al,
wherein the content of Ni and the total content of Cu+Al satisfies the following relationship:

$$Ni \geq (Cu+Al).$$

[0014] In the Fe-Mn-Si alloy, optimizing the contents of constituent elements results in volume contraction which occurs through a martensite transformation ($\gamma \rightarrow \varepsilon$) upon cooling and in volume expansion which occurs through the reverse transformation ($\varepsilon \rightarrow \gamma$) upon heating. The shape changes accompanied by the expansion/contraction are reversible and the amounts of the shape changes are relatively large. Furthermore, the shape-recovery temperature thereof is higher than those of Ti-Ni alloys (specifically, 90-100°C or higher), and the accuracy of shape recovery thereof is high.
In addition, the Fe-Mn-Si alloy having the given composition is inexpensive and has strength which enables the alloy to withstand repetitions of shape recovery. In particular, the strength is further improved by adding a substitutional solid-solution strengthening element such as Mo, or a precipitation strengthening element such as Cu.
Consequently, the two-way shape-recovery alloy of the invention can be used in various functional parts required to have two-way working properties.
[0015] The two-way shape-recovery alloy of the invention can be used as, e.g., a switch or actuator which works based on temperature changes, an expander for a piston ring, and a temperature-sensitive member for use in the oil supply mechanism of a viscous-fluid coupling.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016]

Fig. 1 is a presentation showing the changes in length of a eutectoid steel (0.77 mass% carbon) with changing temperature and with phase transformations.
Fig. 2 is a presentation showing a heating-cooling transformation curve for the alloy of Example 7.
Fig. 3 is a presentation showing the relationship between A_f - M_s and A_s in the alloys of the Examples and Comparative

Examples.

Fig. 4 shows the results of a thermal fatigue test of the alloy obtained in Example 2.

BEST MODE FOR CARRYING OUT THE INVENTION

[0017] One embodiment of the invention is explained below in detail. 1. Two-Way Shape-Recovery Alloy

The two-way shape-recovery alloy of the invention contains the elements shown below, with the remainder being iron and unavoidable impurities, and has a component balance which satisfies a given requirement. The kinds of the additive elements, ranges of the contents thereof, and reasons for the limitations are as follows. Herein, in the present specification, all the percentages defined by mass are the same as those defined by weight, respectively.

In the invention, the term "two-way shape recovery" means that an alloy is caused to reversibly take a low-temperature-state shape and a high-temperature-state shape by mainly utilizing the expansion and contraction which are accompanied by phase transformations, without substantially utilizing a plastic deformation.

[0018] 1.1. Main Constituent Elements

$$(1)\ C < 0.20\ \text{mass\%}$$

Carbon is present as an interstitial element in the iron and is a potent austenite-forming element. In ordinary steel, carbon forms the α' (BCT) phase upon quench-hardening and this leads to an improvement in strength. However, the FCC-BCT transformation is a transformation which accompanies volume expansion. Furthermore, since this transformation highly depends on the cooling rate of material, a change in cooling rate results in the formation of a bainite structure or ferrite structure, thereby making it impossible to obtain stable volume expansion. Moreover, this transformation does not produce a two-way shape-recovery effect.

Consequently, in order for an alloy to exert a two-way shape-recovery effect, the alloy should be prevented from generating the α' phase upon quench-hardening. Accordingly, the alloy must have a carbon content lower than 0.20 mass%. The carbon content thereof is more preferably lower than 0.10 mass%.

$$(2)\ 13.00 \leq Mn \leq 30.00\ \text{mass\%}$$

[0019] Manganese is an additive element which is essential for stably attaining the two-way transformations between γ and ε. At high temperatures, manganese functions as an austenite-forming element. The higher the content of manganese is, the more the ε martensite is apt to generate at low temperatures. From the standpoint of generating ε martensite, the content of manganese must be 13.00 mass% or higher. The content of manganese is more preferably 15.00 mass% or higher.

On the other hand, in case where the manganese content is excessively high, the result is a considerably lowered transformation temperature in cooling and there is a possibility that the austenite phase might be a stable phase even at -50°C. Consequently, the content of manganese must be 30.00 mass% or lower. The content of manganese is more preferably lower than 25.00 mass%.

$$(3)\ 0.10 \leq Si \leq 6.00\ \text{mass\%}$$

[0020] Silicon is an element which reduces stacking-fault energy to accelerate the transformation from the γ phase to the ε phase. From this standpoint, the content of silicon must be 0.10 mass% or higher. The content of silicon is more preferably 0.30 mass% or higher.

On the other hand, in case where the silicon content is excessively high, the strengthening by solid-solution formation is significant and this leads to a decrease in material ductility. Consequently, the content of silicon must be 6.00 mass% or lower. The content of silicon is more preferably 4.00 mass% or lower.

$$(4)\ 0.05 \leq Cr \leq 12.00\ \text{mass\%}$$

[0021] Chromium has the function of controlling the temperature at which the transformation from the γ phase to the ε phase occurs, and further has the function of improving the corrosion resistance of the material. From the standpoint of obtaining such effects, the content of chromium must be 0.05 mass% or higher.
On the other hand, chromium functions as an α-stabilizing element at high temperatures. Therefore, an excessively high chromium content tends to convert a heat-treated structure into an α' martensite structure. Consequently, the content of chromium must be 12.00 mass% or lower.

$$(5)\ 0.01 \leq \mathrm{Ni} \leq 3.00\ \mathrm{mass\%}$$

[0022] Nickel has the function of regulating transformation temperatures without causing a structural change in a heat treatment. From the standpoint of obtaining this effect, the content of nickel must be 0.01 mass% or higher.
On the other hand, nickel is a potent austenite-forming element. Therefore, an excessively high nickel content results in a structural change. Consequently, the content of nickel must be 3.00 mass% or lower.

$$(6)\ \mathrm{N} < 0.100\ \mathrm{mass\%}$$

[0023] Nitrogen combines with aluminum and other elements to form nitrogen compounds and thereby adversely-influences hot workability or cold workability. Furthermore, nitrogen functions as an interstitial element to form a solid solution in the iron and serves as a potent austenite-forming element. As in the case of carbon, an excessively high nitrogen content changes transformation behavior and results in the formation of the α' (BCT) phase in quench-hardening. Consequently, in order for exerting a two-way shape-recovery effect, it is necessary to prevent the alloy from generating the α' phase upon quench-hardening. From this standpoint, the content of nitrogen must be lower than 0.100 mass%. The content of nitrogen is more preferably lower than 0.050 mass%.

1.2. Unavoidable Impurities

[0024] The unavoidable impurities specifically include the followings.

$$(1)\ \mathrm{P} < 0.050\ \mathrm{mass\%}$$

Phosphorus unavoidably comes into the alloy from raw materials. Phosphorus is an element which segregates at grain boundaries to reduce the hot workability of the material. It is therefore preferred to reduce the content of phosphorus to be lower than 0.050 mass%. The content of phosphorus is more preferably lower than 0.010 mass%.

$$(2)\ \mathrm{S} < 0.100\ \mathrm{mass\%}$$

[0025] Sulfur unavoidably comes into the alloy from raw materials. Sulfur segregates at grain boundaries to impair hot workability. In the invention, since the alloy has a high manganese content, the sulfur which has come into the alloy forms MnS and hence exerts a limited influence on hot workability. However, the smaller the sulfur amount is, the more the alloy is preferred. It is therefore preferred to reduce the content of sulfur to be lower than 0.100 mass%. The content of sulfur is more preferably lower than 0.050 mass%.

$$(3)\ \mathrm{O} < 0.050\ \mathrm{mass\%}$$

[0026] Oxygen unavoidably comes into the steel. Oxygen combines with aluminum and silicon to form oxides and thereby adversely influences hot workability or cold workability. It is therefore preferred to reduce the content of oxygen to be lower than 0.050 mass%. The content of oxygen is more preferably lower than 0.020 mass%.

(4) Mo < 0.10 mass%

(5) W < 0.10 mass%

(6) V < 0.05 mass%

(7) Co < 0.10 mass%

[0027] Molybdenum, tungsten, vanadium, and cobalt each may unavoidably come into the steel. Although these elements do not exert a considerable influence on transformation temperatures or the type of structure, it is preferred to reduce the contents thereof to be lower than the values shown above.
Incidentally, these elements each function as a substitutional solid-solution strengthening element. In such a case, the elements may be added in amounts not smaller than the values shown above. This respect will be described later.

(8) Cu < 0.10 mass%

[0028] Copper is an element which unavoidably comes into the alloy from raw materials. Excessively high copper contents cause the alloy to show red shortness, and considerably impair the processability thereof. From the standpoint of maintaining processability, it is preferred to reduce the content of copper to be lower than 0.10 mass%. The content of copper is more preferably lower than 0.05 mass%.
Incidentally, it is possible to positively add copper, on condition that a given amount nickel should be added, to thereby conduct precipitation strengthening based on the secondary precipitation of copper. In such a case, a copper content of up to 1.00 mass% is allowable. This respect will be described later.

(9) Al < 0.10 mass%

[0029] Aluminum unavoidably comes into the alloy because it is used as a deoxidizer like silicon. Aluminum combines with oxygen to form an oxide and thereby adversely influences hot workability or cold workability. It is therefore preferred to reduce the content of aluminum to be lower than 0.10 mass%.
Incidentally, it is possible to positively add aluminum, on condition that a given amount of nickel should be added, to thereby improve strength based on the secondary precipitation of an Al-Ni intermetallic compound. In such a case, an aluminum content of up to 1.00 mass% is allowable. This respect will be described later.

1.3. Component Balance

[0030] The two-way shape-recovery alloy of the invention must satisfy the following expression (1) besides the requirement that the contents of component elements should be the respective ranges shown above.

$$600 \leq 33Mn + 11Si + 28Cr + 17Ni \leq 1050 \qquad (1)$$

[0031] The value determined from expression (1) correlates with the transformation temperatures of the alloy, and is an experiential value. By optimizing the component balance among manganese, silicon, chromium, and nickel, the γ phase can be stably ensured at a high temperature (300°C or higher) and the ε phase can be stably ensured at a low temperature (-50°C or lower), respectively.

As stated above, manganese mainly serves as an austenite-forming element and also functions as an element which forms the ε phase upon cooling. Silicon accelerates the conversion of the γ phase to the ε phase at low temperatures but functions as an α-stabilizing element at high temperatures. Although chromium functions as an α-stabilizing element at high temperatures, it is an element effective in controlling the temperatures at which the γ phase transforms to the ε phase. Nickel is an element effective in controlling the temperatures at which the γ phase transforms to the ε phase.

[0032] The smaller the value of expression (1) is, the higher the transformation finish temperature in heating (A_f point) is. In case where the A_f point is too high, there is a possibility that a creep deformation might occur during the reverse transformation (ε→γ), resulting in reduced accuracy of shape recovery. In order for obtaining high accuracy of shape recovery, it is necessary that the A_f point should be 400°C or lower. From the standpoint of attaining this, the value of expression (1) must be 600 or larger. The value of expression (1) is more preferably 700 or larger.

On the other hand, the larger the value of expression (1) is, the lower the transformation start temperature in heating (A_s point) is. In case where the value of expression (1) becomes too large, the A_s point becomes room temperature or lower and it becomes difficult to cause this alloy to undergo shape recovery at a temperature higher than the shape-recovery temperatures of Ti-Ni alloys. From the standpoints of attaining an A_s point which is higher than the shape-recovery temperatures of Ti-Ni alloys and thereby enabling the alloy of the invention to undergo shape recovery at a temperature of 90-100°C or higher, the value of expression (1) must be 1,050 or smaller. The value of expression (1) is more preferably 900 or smaller.

1.4. Transformation Temperatures

[0033] A martensite transformation (γ→ε) starts at a transformation start temperature in cooling (M_s point) and is finished at a transformation finish temperature is cooling (M_f point). On the other hand, the reverse transformation (ε→γ) starts at a transformation start temperature in heating (A_s point) and is finished at a transformation finish temperature in heating (A_f point).

As stated above, the A_s point can be elevated to 90°C or higher, or 100°C or higher, by optimizing the value of expression (1).

[0034] In the case where a two-way shape-recovery effect is applied to a device required to have two-way working properties, it is desirable that reversible shape changes should occur in a narrow temperature range. Namely, the smaller the difference (A_f - M_s) between the transformation finish temperature in heating (A_f) and the transformation start temperature in cooling (M_s) is, the better the alloy is. In general, the value of A_f - M_s in low-alloy steels is 200-300°C or larger. In contrast, in the two-way shape-recovery alloy of the invention, the value of A_f - M_s can be reduced to 200-300°C or smaller by optimizing the contents of the component elements, such as Mn and Si, which influence the transformation temperature. From the standpoint of reducing the size of the hysteresis loop accompanying heating/cooling, the value of A_f - M_s is preferably 150°C or smaller. The value of A_f - M_s is more preferably 100°C or smaller.

Incidentally, each transformation temperature can be determined by drawing a tangent to an expansion-contraction curve at each of points respectively located before and after the area where the inclination of the curve changes and taking the temperature corresponding to the point of intersection of these tangents as the transformation temperature.

1.5. Minor Constituent Elements

[0035] The two-way shape-recovery alloy of the invention may further contain one or more of the following elements besides the elements described above.

1.5.1 Substitutional Solid-Solution Strengthening Elements

[0036]

$$(1)\ 0.10 \leq \mathrm{Mo} \leq 2.00\ \mathrm{mass\%}$$

$$(2)\ 0.10 \leq \mathrm{W} \leq 2.00\ \mathrm{mass\%}$$

$$(3)\ 0.05 \leq \mathrm{V} \leq 1.00\ \mathrm{mass\%}$$

$$(4)\ 0.10 \leq Co \leq 5.00\ mass\%$$

In the case where the two-way shape-recovery alloy of the invention is desired to be improved in strength, a substitutional solid-solution strengthening element can be added thereto so long as this exerts no influence on the transformation behavior exhibited by the alloy upon heating/cooling. Examples of the substitutional solid-solution strengthening element include molybdenum, tungsten, vanadium, and cobalt. Any one of these elements may be added, or two or more thereof may be added.

From the standpoint of attaining the solid solution strengthening, it is preferred that the contents of molybdenum, tungsten, vanadium, and cobalt should be not lower than the respective lower limits shown above, respectively.

On the other hand, when the contents of these elements are excessively high, not only the effect is not enhanced any more or an increased cost results but also there are cases where such high contents thereof influence transformation behavior. It is therefore preferred that the contents of these elements should be not higher than the respective upper limits shown above, respectively.

1.5.2. Precipitation Strengthening Elements

[0037]

$$(5)\ 0.10 \leq (Cu+Al) \leq 1.00\ mass\%$$

$$(6)\ Ni \geq (Cu+Al)$$

[0038] In case where copper is added alone, the copper precipitates at grain boundaries to reduce hot workability. However, when a given amount of nickel is added simultaneously with the addition of copper, the nickel inhibits the copper from precipitating at grain boundaries. As a result, the copper undergoes secondary precipitation within the grains to improve strength.

From the standpoint of obtaining this effect, it is preferred to regulate the content of copper to 0.10 mass% or higher. On the other hand, an excessively high copper content results in a decrease in hot workability. It is therefore preferred to regulate the content of copper to 1.00 mass% or lower.

From the standpoint of attaining precipitation strengthening without reducing hot workability, it is preferred to add nickel in an amount equal to or larger than the copper amount. More preferably, the nickel amount is at least two times the copper amount.

[0039] Likewise, in case where aluminum is added alone, an oxide generates in a large amount to reduce hot workability or cold workability. However, when a given amount of nickel is added simultaneously with the addition of aluminum, the secondary precipitation of an Ni-Al intermetallic compound occurs to improve strength.

From the standpoint of obtaining this effect, it is preferred to regulate the content of aluminum to 0.10 mass% or higher. On the other hand, an excessively high aluminum content results in a decrease in hot workability on cold workability. It is therefore preferred to regulate the content of aluminum to 1.00 mass% or lower.

From the standpoint of attaining precipitation strengthening without reducing hot workability or cold workability, it is preferred to add nickel in an amount equal to or larger than the aluminum amount. More preferably, the nickel amount is at least two times the aluminum amount.

[0040] Furthermore, it is possible to simultaneously add copper and aluminum, on condition that a given amount of nickel should be added, to thereby attain precipitation strengthening with both the copper and the aluminum. From the standpoint of obtaining this effect, it is preferred to regulate the total content of copper and aluminum to 0.1 mass% or higher.

On the other hand, from the standpoint of inhibiting hot workability and cold workability from decreasing, it is preferred to regulate the total content of copper and aluminum to 1.00 mass% or lower.

Also in the case of simultaneously adding copper and aluminum, it is preferred to add nickel in an amount equal to or larger than the total amount of the copper and the aluminum. More preferably, the nickel amount is at least two times the sum of the copper and the aluminum.

[0041] In this regard, with regard to each element contained in the alloy of the invention, according to an embodiment, the minimal amount thereof present in the alloy is the smallest non-zero amount used in the Examples of the developed

alloys as summarized in Tables 1 and 2. According to a further embodiment, the maximum amount thereof present in the alloy is the maximum amount used in the Examples of the developed alloys as summarized in Tables 1 and 2.

2. Functional Parts Employing the Two-Way Shape-Recovery Alloy

[0042] The two-way shape-recovery alloy of the invention has the function of reversibly taking a low-temperature-state shape and a high-temperature-state shape based on the expansion/contraction which are accompanied by the transformation between γ and ε, without substantially using a plastic deformation.

[0043] Therefore, the two-way shape-recovery alloy having such function can be applied to functional parts such as:

(1) a switch or actuator which takes advantage of changes between a high-temperature-state shape and a low-temperature-state shape,
(2) an actuator having a mechanism in which the shape recovery deflection accompanying a temperature change is amplified on the principle of a sprig or lever,
(3) a switch or actuator required to have a shape-recovery temperature of 100°C or higher,
(4) an expander for a piston ring (see, for example, International Publication WO 2004/090318), and
(5) a temperature-sensitive member for use in the oil supply mechanism of a viscous-fluid coupling device (see, for example, JP-A-11-264425).

[0044] Although the two-way shape-recovery alloy of the invention can be used as it is, the alloy may be used after the surface thereof is subjected to any of various surface treatments. Examples of the surface treatments include nitriding, PVD, and CVD. By such surface treatments, oxidation resistance and wearing resistance can be imparted.
The two-way shape-recovery alloy to which wearing resistance has been imparted by a surface treatment can be applied to a mechanical part (e.g., a coil spring, piston ring, or the like) which is used in the state of being in contact with a mating material.

3. Process for Producing the Two-Way Shape-Recovery Alloy

[0045] The two-way shape-recovery alloy of the invention can be produced by melting raw materials which have been mixed together in a given proportion and then casting the melt. It is preferred that, after the cast is forged to impart a given shape thereto, the forged alloy is subjected to a solution heat treatment (ST treatment) and subsequent air cooling in order to eliminate the influence of the forging. The temperature for the solution heat treatment is preferably 700-1,200°C. In the case where a precipitation strengthening element has been added, it is preferred to conduct an aging treatment after a solution heat treatment and subsequent air cooling. It is preferred that the aging treatment is conducted at a temperature of from 400°C to 600°C for a period of from 0.5 hours to less than 5 hours.

4. Functions of the Two-Way Shape-Recovery Alloy

[0046] In Fig. 1 is shown the changes in length of a eutectoid steel (0.77 mass% carbon) with changing temperature and with phase transformations.
At a temperature around room temperature (point A), the eutectoid steel has a ferrite (α) phase structure. When heated to an austenite (γ) phase region, this eutectoid steel undergoes expansion → contraction → expansion along the curve A→B→C→D as shown in Fig. 1. Further, when this eutectoid steel is gradually cooled from the γ-phase region to room temperature, the eutectoid steel undergoes contraction → expansion → contraction along the curve D→E→F→A and returns to the shape which the steel possessed before the heating. The reason why the eutectoid steel contracts along the curve B→C during heating is that an α→γ transformation occurs. The reason why the eutectoid steel expands along the curve E→F during cooling in that a γ→α transformation occurs.

[0047] On the other hand, when the eutectoid steel is rapidly cooled from the γ-phase region, this steel undergoes contraction → expansion along the broken-line curve (curve D-H) as shown in Fig. 1 and comes to have a shape different from the shape of steel before the heating. When the eutectoid steel which has been rapidly cooled is heated again, this eutectoid steel repeatedly undergoes expansion and contraction along the curve H→J→K→L→M→N→O and finally reaches point D.
The reason why the length of the steel as measured after the rapid cooling (point H) is larger than the length of the steel as measured before the heating (point A) is that the rapid cooling of the eutectoid steel from the γ-phase region to a temperature not higher than the M_s point results in a martensite transformation (γ (FCC) → α' (BCT) transformation) which accompanies volume expansion. Furthermore, the reason why the expansion or contraction occurring at temperatures of 400°C and lower is larger than the change in length resulting from thermal expansion is that ε-carbide formation, residual-γ decomposition, and θ-carbide formation occur with the increase of the temperature.

[0048] In iron-based alloys for general use, the martensite transformation which is caused by such a heat treatment and the reverse transformation are positively used for structure control.
However, since the $\gamma \rightarrow \alpha'$ transformation, which occurs upon cooling, accompanies volume expansion, general iron-based alloys cannot be used as shape-recovery alloys required to contract upon cooling.
The $\gamma \rightarrow \alpha'$ transformation highly depends on the cooling rate of the material. Therefore, a change in cooling rate may result in the formation of a bainite structure or ferrite structure and stable volume expansion (i.e., reproducibility of shape recovery) cannot be obtained.
Furthermore, the $\alpha \rightarrow \gamma$ transformation finish temperature in heating (A_f point) is as high as 700°C or above. Moreover, the difference between the A_f point and the $\gamma \rightarrow \alpha'$ transformation start temperature in cooling (M_s point) is as large as 200-300°C or more. Namely, the hysteresis loop accompanying heating/cooling is large.

[0049] In contrast, the two-way shape-recovery alloy of the invention comprises an Fe-Mn-Si alloy as the base, and the contents of the component elements therein are optimized. Therefore, when this alloy is cooled from a high temperature (300°C or higher) to a low temperature (-50°C or lower), a transformation occurs from the γ (FCC) phase to the ε (HCP) phase and neither the α (BCC) phase nor the α' (BCT) phase generates. Since the $\gamma \rightarrow \varepsilon$ transformation causes volume contraction, the cooling results in contraction to a degree higher than the shape change accompanied by thermal contraction.
On the other hand, when this alloy is heated, the $\varepsilon \rightarrow \gamma$ transformation occurs. The heating hence results in expansion to a degree higher than the shape change accompanied by thermal expansion. In addition, the changes in shape accompanied by the expansion/contraction are reversible. No plastic deformation is hence necessary for shape recovery.

[0050] Furthermore, the two-way shape-recovery alloy of the invention shows a relatively large shape change amount. Specifically, by optimizing the component elements, the degree of change in length ($\Delta L/L_0 \times 100$) in heating becomes 0.3% or higher, preferably 0.5% or higher, more preferably 0.7% or higher. By optimizing the shape of this two-way shape-recovery alloy (e.g., shaping the alloy into a spring), that shape change amount can be further increased.
On the other hand, the degree of change in length in cooling is the same as the degree of change in length in heating. Specifically, the degree of change in length per heating/cooling cycle is 0.1 % or lower, and the degree of shape recovery is exceedingly high. Even when a heating/cooling cycle is repeated several hundred times, the rate of shape recovery hardly deteriorates with the lapse of time.

[0051] Moreover, since the two-way shape-recovery alloy of the invention comprises an Fe-Mn-Si alloy as the base, the shape-recovery temperature (A_s point) is higher than those of conventional Ti-Ni alloys. Since the component elements have been optimized, the hysteresis loop accompanying heating/cooling (A_f - M_s) is smaller than those of general iron-based alloy.
Specifically, when the component elements are optimized so that expression (1) is satisfied, the A_s point becomes 90°C or higher, preferably 100°C or higher. Likewise, when the component elements are optimized so that expression (1) is satisfied, the value of A_f - M_s becomes 200°C or smaller, preferably 150°C or smaller, more preferably 100°C or smaller.

[0052] In addition, since the two-way shape-recovery alloy of the invention comprises an Fe-Mn-Si alloy as the base, it is inexpensive and has strength which enables the alloy to withstand repetitions of shape recovery. In particular, the strength is further improved by adding a substitutional solid-solution strengthening element such as Mo or a precipitation strengthening element such as Cu.
Consequently, the two-way shape-recovery alloy of the invention can be used in various functional parts required to have two-way working properties. Examples

(EXAMPLES 1 TO 28 AND COMPARATIVE EXAMPLES 1 TO 10)

1. Production of Samples

[0053] Each of the materials respectively having the chemical compositions shown in Table 1 and Table 2 (50 kg each) was melted in a high-frequency-heating melting furnace, followed by casting. The casts obtained were respectively subjected to soaking at 1,200°C for 24 hours, subsequently forged to ϕ 30 mm at a temperature of 800°C or higher, and then gradually cooled. In order to eliminate the influence of the forging conditions, etc., the resultant forged alloys were respectively subjected to a solution heat treatment at 800°C for 30 minutes and then air-cooled.
Furthermore, with respect to Examples 10 to 13, in which 0.1 mass% or more copper had been added, and Examples 14 to 18, in which 0.1 mass% or more aluminum had been added, an aging treatment was conducted after the solution heat treatment and the air cooling. The aging treatment was conducted at a temperature of 500°C for a period of 1.5 hours.

[0054]

Table 1

	Composition (mass%)														
	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	W	V	Co	Al	O	N
Example 1	0.10	1.24	19.12	0.011	0.042	0.06	0.01	1.45	0.08	0.10	0.02	0.07	0.039	0.028	0.092
Example 2	0.08	5.24	15.37	0.034	0.033	0.02	1.34	11.81	0.07	0.01	0.05	0.08	0.064	0.010	0.063
Example 3	0.11	0.72	19.55	0.023	0.004	0.03	0.64	3.11	0.04	0.06	0.00	0.04	0.021	0.027	0.090
Example 4	0.01	0.32	15.99	0.044	0.010	0.03	1.98	6.33	0.05	0.00	0.00	0.06	0.090	0.019	0.013
Example 5	0.04	5.24	22.12	0.031	0.017	0.09	1.66	5.81	0.05	0.03	0.05	0.02	0.078	0.044	0.060
Example 6	0.05	4.01	19.02	0.024	0.042	0.05	0.77	3.42	0.06	0.06	0.01	0.01	0.018	0.041	0.036
Example 7	0.15	5.09	14.42	0.015	0.042	0.06	1.87	8.99	0.00	0.07	0.02	0.01	0.006	0.027	0.049
Example 8	0.01	1.09	18.33	0.009	0.041	0.01	0.78	11.18	0.03	0.05	0.04	0.08	0.023	0.030	0.093
Example 9	0.08	0.90	14.51	0.024	0.042	0.05	1.50	5.41	0.01	0.05	0.03	0.09	0.037	0.040	0.043
Example 10	0.02	3.84	20.28	0.010	0.022	0.71	0.98	3.20	0.25	0.09	0.02	0.09	0.001	0.019	0.078
Example 11	0.11	1.11	20.68	0.007	0.050	0.46	0.74	8.90	0.02	0.04	0.02	0.07	0.027	0.009	0.013
Example 12	0.17	3.80	16.06	0.014	0.003	0.63	1.46	11.06	0.04	0.01	0.01	0.07	0.045	0.004	0.098
Example 13	0.13	3.79	15.57	0.020	0.032	0.69	2.38	7.82	0.01	0.04	0.02	0.02	0.038	0.006	0.098
Example 14	0.10	2.08	18.01	0.021	0.033	0.08	2.95	11.87	0.08	0.03	0.03	0.06	0.639	0.033	0.036
Example 15	0.05	2.67	19.02	0.028	0.045	0.02	3.00	0.93	0.03	0.06	0.00	0.00	0.604	0.032	0.040
Example 16	0.03	1.34	21.39	0.020	0.044	0.01	1.95	3.98	0.00	0.06	0.00	0.03	0.966	0.027	0.026
Example 17	0.17	5.42	24.97	0.007	0.007	0.32	0.98	4.55	0.04	0.09	0.01	0.05	0.263	0.027	0.066
Example 18	0.17	3.03	16.78	0.034	0.041	0.05	2.69	4.21	0.05	0.08	0.01	0.07	0.433	0.032	0.069
Example 19	0.14	1.22	14.84	0.027	0.018	0.00	1.53	6.39	0.59	0.77	0.02	0.06	0.002	0.019	0.063
Example 20	0.16	1.11	17.75	0.035	0.039	0.05	1.94	3.81	0.08	0.06	0.25	1.15	0.044	0.035	0.084
Example 21	0.16	0.77	21.00	0.036	0.030	0.05	0.33	2.94	0.10	1.99	0.05	0.05	0.041	0.011	0.013
Example 22	0.13	3.15	24.07	0.039	0.034	0.03	1.48	1.68	0.02	0.04	0.02	4.86	0.080	0.014	0.016
Example 23	0.16	5.83	19.44	0.019	0.008	0.01	1.42	0.34	0.01	0.07	0.96	0.09	0.070	0.038	0.038
Example 24	0.10	5.45	27.06	0.047	0.001	0.06	1.36	1.25	1.88	0.03	0.01	3.22	0.072	0.047	0.090

(continued)

	Composition (mass%)													
	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	W	V	Co	Al	O	N
Example 25	0.19	4.86	13.64	0.013	0.047	0.04	1.99	7.33	0.09	1.33	0.52	0.00	0.070	0.018	0.006

[0055]

Table 2

	Composition (mass%)														
	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	W	V	Co	Al	O	N
Example 26	0.03	2.11	27.21	0.010	0.046	0.01	1.22	3.02	1.12	0.03	0.02	2.33	0.063	0.034	0.041
Example 27	0.09	1.64	18.84	0.024	0.017	0.09	1.90	2.80	0.34	0.50	0.22	0.54	0.012	0.004	0.064
Example 28	0.06	0.95	16.26	0.049	0.045	0.04	0.25	4.21	0.08	1.68	0.04	0.07	0.020	0.033	0.070
Comparative Example 1	0.02	0.31	22.11	0.011	0.034	0.02	0.02	12.10	0.03	0.01	0.02	0.01	0.021	0.011	0.004
Comparative Example 2	0.02	6.17	28.09	0.021	0.023	0.08	0.15	5.01	0.01	0.02	0.01	0.02	0.033	0.022	0.018
Comparative Example 3	0.02	4.43	22.11	0.011	0.034	0.02	0.02	12.10	0.03	0.01	0.02	0.01	0.021	0.01	0.004
Comparative Example 4	0.05	0.49	0.71	0.022	0.021	0.04	9.22	18.02	0.06	0.08	0.03	0.02	0.024	0.017	0.022
Comparative Example 5	0.33	0.38	0.62	0.016	0.017	0.09	0.02	13.33	1.01	0.01	0.02	0.03	0.033	0.043	0.033
Comparative Example 6	0.05	3.98	8.12	0.024	0.042	0.05	0.22	3.11	0.06	0.06	0.01	0.01	0.018	0.041	0.036
Comparative Example 7	0,05	4.01	11.11	0.024	0.042	0.05	0.02	3.42	0.06	0.06	0.01	0.01	0.018	0.041	0.036
Comparative Example 8	0.05	4.41	33.22	0.024	0.042	0.05	0.06	3.23	0.06	0.06	0.01	0.01	0.018	0.041	0.036
Comparative Example 9	0.05	3.97	13.55	0.024	0.042	0.05	0.23	22.14	0.06	0.06	0.01	0.01	0.018	0.041	0.036
Comparative Example 10	0.10	0.81	13.55	0.023	0.043	1.01	2.23	18.33	1.01	0.01	0.01	0.01	0.043	0.063	0.410

2. Test Methods

2.1. Transformation Temperatures and Degree of Change in Length

[0056] A differential dilatometer was used to determine transformation - temperatures in heating/cooling (As, A_f, M_s, and M_f) and the degree of the change in length occurring with the transformation in heating (coefficient of expansion). The size of each test piece was ϕ5 mm $\times$ 20 mm, the rate of heating was 10 °C/min, and the rate of cooling was 10 °C/min.

2.2. Structure

[0057] A sample which had been held at -50°C was subjected to X-ray diffractometry to identify the phase. As the X-ray was used the K_α line of cobalt.

2.3. Thermal Fatigue Test

[0058] A test piece having a parallel-part length of 40 mm was subjected to a thermal fatigue test. A strain measurement part (region having a length of 15 mm) in the parallel part of the test piece was heated and, at the time when a maximum temperature was reached, both ends of the test piece was fixed. The test piece in this state was subjected to 300 repetitions of a cooling/heating cycle to examine the relationship between the temperature change and the stress generated in the test piece. The maximum temperature and minimum temperature were set at 300°C and 50°C, respectively. The rate of heating was 250 °C/min on average, and the rate of cooling was 83 °C/min on average.

2.4. Tensile Test

[0059] Tensile test was carried out using a JIS 14A (M18) sample. Conditions of the tensile test were in accordance with JIS Z2241.

3. Results

3.1. Transformation Temperatures, Degree of Change in Length, and Structure

[0060] In Table 3 are shown the degree of change in length with transformation in heating ($\Delta L/L_0 \times 100$), A_f - M_s, A_s, the value of expression (1), and the structure observed at -50°C.

[0061]

Table 3

	$\Delta L/L_0$ (%)	A_f - M_s (°C)	A_s (°C)	Expression (1)	Structure (at -50°C)
Example 1	0.88	168	234	685	ε
Example 2	0.55	145	154	918	ε
Example 3	0.79	180	234	751	ε
Example 4	0.80	132	233	742	ε
Example 5	0.47	103	121	979	ε+γ
Example 6	0.75	189	198	781	ε
Example 7	0.70	195	207	815	ε
Example 8	0.52	134	145	943	ε+γ
Example 9	0.91	230	251	666	ε
Example 10	0.70	141	195	818	ε
Example 11	0.50	127	138	956	ε+γ
Example 12	0.57	152	161	906	ε+γ
Example 13	0.70	149	193	815	ε
Example 14	0.44	92	98	1000	ε+γ

(continued)

	$\Delta L/L_0$ (%)	$A_f - M_s$ (°C)	A_s (°C)	Expression (1)	Structure (at -50°C)
Example 15	0.81	189	232	734	ε
Example 16	0.66	166	185	865	ε
Example 17	0.42	98	104	1028	ε+γ
Example 18	0.79	202	223	751	ε
Example 19	0.85	211	233	708	ε
Example 20	0.81	207	243	738	ε
Example 21	0.74	189	201	789	ε
Example 22	0.58	149	155	901	ε+γ
Example 23	0.80	214	234	739	ε
Example 24	0.42	103	119	1011	ε+γ
Example 25	0.80	203	221	743	ε
Example 26	0.40	89	108	1026	ε+γ
Example 27	0.79	211	231	750	ε
Example 28	0.90	246	257	669	ε
Comparative Example 1	0.34	183	56	1072	γ+ε
Comparative Example 2	0.25	135	45	1138	γ+ε
Comparative Example 3	0.28	699	674	1118	α+ε
Comparative Example 4	0.87			690	γ
Comparative Example 5	1.28	320	665	398	α
Comparative Example 6	1.28	469	654	403	α
Comparative Example 7	1.13	354	333	507	ε+α
Comparative Example 8	0.11	228	32	1236	ε
Comparative Example 9	0.28	397	632	1115	α' martensite
Comparative Example 10	0.43			1007	γ

[0062] Comparative Example 1 (JST) and Comparative Example 2 (NSC) were low in A_s because the values of expression (1) exceeded 1,050. Comparative Example 3 (JST-2) had a value of $A_f - M_s$ exceeding 600°C and generated the α phase upon cooling, because the chromium content was excessively high and the value of expression (1) exceeded 1,050.

Comparative Example 4 (corresponding to SUS304) contained only the γ phase even at -50°C because the nickel content was excessively high. Comparative Example 5 (SUS420), Comparative Example 6, and Comparative Example 7 generated the α phase because each alloy had an improper component balance.

Comparative Example 8 was low in A_s because the value of expression (1) exceeded 1,050. Comparative Example 9 generated the α' phase because the chromium content was excessively high. Furthermore, Comparative Example 10 contained only the γ phase even at -50°C because the nitrogen content was excessively high.

[0063] In contrast, Examples 1 to 28 at -50°C each contained the ε phase and contained neither the α phase nor the α' phase, because the components had been optimized. The degree of change in length during heating was 0.3% or higher in each Example. The value of $A_f - M_s$ was 300°C or smaller in each Example, and A_s was 90°C or higher in each Example.

[0064] In Fig. 2 is shown a heating-cooling transformation curve for the alloy of Example 7. It can be seen from Fig. 2 that transformations between γ and ε occur during heating/cooling and this results in reversible changes in shape.

In Fig. 3 is shown the relationship between $A_f - M_s$ and A_s in the alloys of the Examples and Comparative Examples. In each of the alloys of the Examples, in which the structure is the ε phase or is constituted of the ε phase and the γ phase, the A_s is on the relatively low-temperature side and the $A_f - M_s$ is relatively small. In contrast, the alloys of the Comparative

Examples including the α phase or α' phase tend to have an A_s of 600°C or higher and a large value of A_f - M_s.

3.2. Thermal Fatigue Test

[0065] In Fig. 4 is shown the relationship between the temperature change and the stress generated in the test piece in the first cycle, 100th cycle, and 300th cycle in the alloy obtained in Example 2.

[0066] It can be seen from Fig. 4 that

(1) throughout the thermal fatigue test, the transformation temperatures in heating (A_s and A_f) and the transformation temperature in cooling (M_s) were almost constant, and
(2) the stress generated was almost constant regardless of the number of repetitions.

It was found from the results given above that the alloys according to the invention exhibit stable characteristics when used as two-way shape-recovery alloys.

3.3. Tensile Test

[0067] Table 4 shows the results of the tensile test. As shown in Table 4, the followings can be seen.

(1) Some of the Comparative Examples were low in strength, while all the Examples 1 to 28 had a strength higher than 800 MPa.
(2) When a certain amount(s) of A1 and/or Cu is/are added in addition to main constituent elements and the aging treatment is then carried out, tensile strength is further improved.
(3) When a certain amount(s) of Mo, W, V and/or Co is/are added, tensile strength is further improved.

[0068]

	Tensile strength (MPa)
Example 1	820
Example 2	873
Example 3	855
Example 4	863
Example 5	903
Example 6	835
Example 7	842
Example 8	863
Example 9	837
Example 10	867
Example 11	887
Example 12	989
Example 13	997
Example 14	1065
Example 15	1013
Example 16	899
Example 17	964
Example 18	997
Example 19	1124
Example 20	946

(continued)

	Tensile strength (MPa)
Example 21	955
Example 22	997
Example 23	948
Example 24	1015
Example 25	976
Example 26	996
Example 27	1004
Example 28	896
Comparative Example 1	834
Comparative Example 2	842
Comparative Example 3	863
Comparative Example 4	630
Comparative Example 5	753
Comparative Example 6	793
Comparative Example 7	673
Comparative Example 8	621
Comparative Example 9	1134
Comparative Example 10	593

[0069] While the invention has been described above in detail with reference to embodiments thereof, the invention should not be construed as being limited to the embodiments in any way. Various modifications can be made in the invention without departing from the spirit of the invention.

[0070] The present application is based on Japanese Application No. 2008-309262 filed on December 4, 2008 and Japanese Application No. 2009-266700 filed on November 24, 2009, the contents thereof being incorporated herein by reference.

Claims

1. A two-way shape-recovery alloy, which comprises:

less than 0.20 mass% of C,
13.00 to 30.00 mass% of Mn,
0.10 to 6.00 mass% of Si,
0.05 to 12.00 mass% of Cr,
0.01 to 3.00 mass% ofNi, and
less than 0.100 mass% of N,
with the remainder being Fe and unavoidable impurities,
wherein the contents of Mn, Si, Cr and Ni satisfy the following expression (1):

$$600 \leq 33Mn + 11Si + 28Cr + 17Ni \leq 1050 \qquad (1).$$

2. The two-way shape-recovery alloy according to claim 1,
wherein the difference (A_f - M_s) between a transformation finish temperature in heating (A_f point) and a transformation

start temperature in cooling (M_s point) is 150°C or smaller, and/or
wherein the alloy has a transformation start temperature in heating (A_s point) of 100°C or higher.

3. The two-way shape-recovery alloy according to claim 1, which further comprises at least one of:

0.10 to 2.00 mass% of Mo,
0.10 to 2.00 mass% of W,
0.05 to 1.00 mass% of V, and
0.10 to 5.00 mass% of Co.

4. The two-way shape-recovery alloy according to claim 2, which further comprises at least one of:

0.10 to 2.00 mass% of Mo,
0.10 to 2.00 mass% of W,
0.05 to 1.00 mass% of V, and
0.10 to 5.00 mass% of Co.

5. The two-way shape-recovery alloy according to claim 1, which further comprises 0.10 to 1.00 mass% of Cu+Al, wherein the content of Ni and the total content of Cu+Al satisfies the following relationship:

$$Ni \geq (Cu+Al).$$

6. The two-way shape-recovery alloy according to claim 2, which further comprises 0.10 to 1.00 mass% of Cu+Al, wherein the content of Ni and the total content of Cu+Al satisfies the following relationship:

$$Ni \geq (Cu+Al).$$

7. The two-way shape-recovery alloy according to claim 3, which further comprises 0.10 to 1.00 mass% of Cu+Al, wherein the content of Ni and the total content of Cu+Al satisfies the following relationship:

$$Ni \geq (Cu+Al).$$

8. The two-way shape-recovery alloy according to claim 4, which further comprises 0.10 to 1.00 mass% of Cu+Al, wherein the content of Ni and the total content of Cu+Al satisfies the following relationship:

$$Ni \geq (Cu+Al)$$

9. The two-way shape-recovery alloy according to claim 1 or 2, further comprising at least one of
up to 2.00 mass% of Mo,
up to 2.00 mass% of W,
up to 1.00 mass% of V,
up to 5.00 mass% of Co, and
up to 1.00 mass% of Cu+Al.

10. The alloy according to one of claims 1 to 9, further comprising:

less than 0.050 mass% P,
less than 0.100 mass% S, and
less than 0.050 mass% O.

11. A method of manufacturing the alloy according to one of the preceding claims, comprising:

- mixing together raw materials in the prescribed proportion;
- melting the mixed raw materials; and
- casting the melt.

12. The method according to claim 11, comprising forging the alloy and subjecting the forged alloy to a solution heat treatment and subsequent air cooling, wherein the temperature for the solution heat treatment is preferably in the range 700-1200°C.

13. The method according to claim 12, comprising conducting an ageing treatment after the solution heat treatment and the air cooling, wherein the ageing treatment is preferably conducted at a temperature of from 400°C to 600°C for a period of preferably from 0.5 hours to less than 5 hours.

14. The method according to one of claims 11 to 13, comprising subjecting the surface of the alloy to a surface treatment such as nitriding, PVD, or CVD.

15. Use of the alloy according to one of claims 1 to 10, or as manufactured according to one of claims 11 to 14, as a switch, actuator, expander for a piston ring, or as a temperature-sensitive member for use e.g. in an oil supply mechanism of a viscous-fluid coupling.

FIG. 1

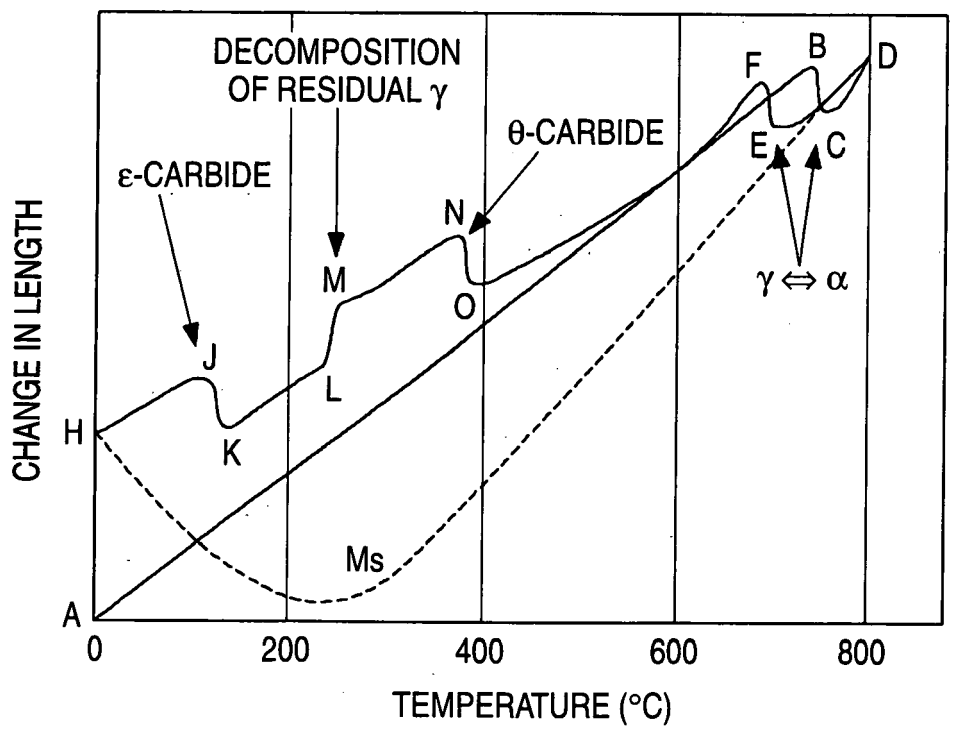

DECOMPOSITION
OF RESIDUAL γ
θ-CARBIDE
ε-CARBIDE
F
B
D
E
C
N
M
O
J
L
K
H
A
Ms
γ ⇔ α
CHANGE IN LENGTH
0
200
400
600
800
TEMPERATURE (°C)

FIG. 2

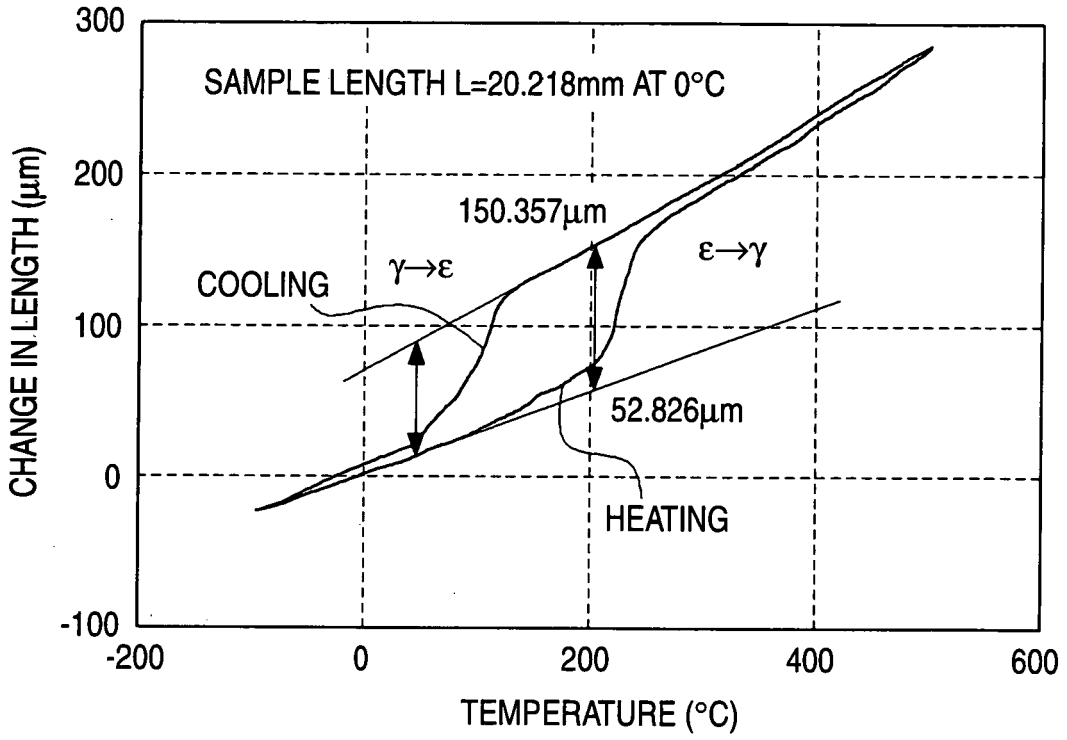

SAMPLE LENGTH L=20.218mm AT 0°C
150.357μm
52.826μm
COOLING
γ→ε
ε→γ
HEATING
CHANGE IN LENGTH (μm)
TEMPERATURE (°C)
300
200
100
0
-100
-200
0
200
400
600

FIG. 3

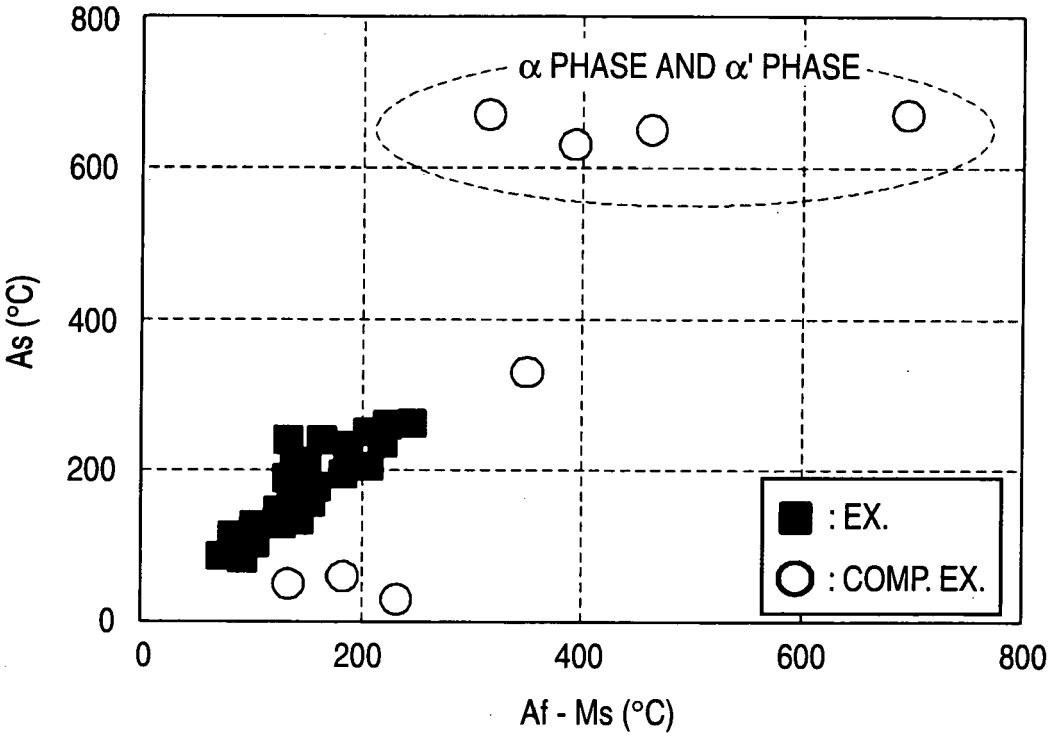
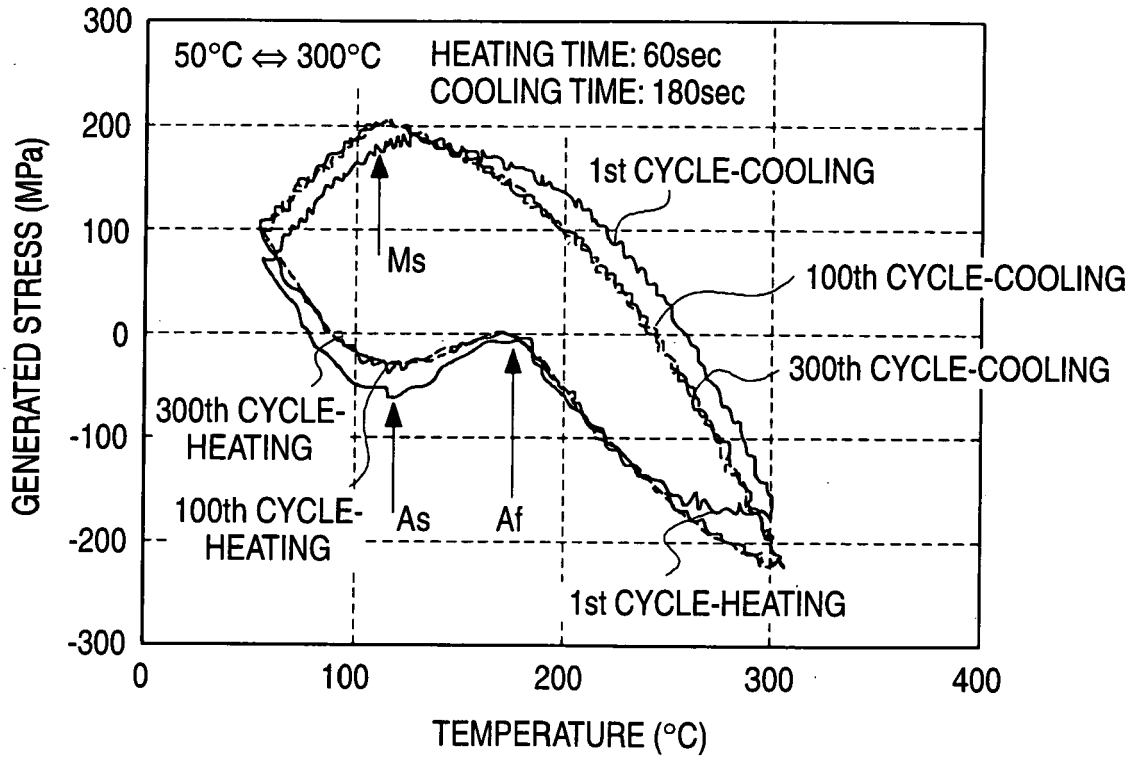

800
600
400
200
0
As (°C)
α PHASE AND α' PHASE
: EX.
: COMP. EX.
0
200
400
600
800
Af - Ms (°C)

FIG. 4


50°C ⇔ 300°C
HEATING TIME: 60sec
COOLING TIME: 180sec
1st CYCLE-COOLING
100th CYCLE-COOLING
300th CYCLE-COOLING
Ms
300th CYCLE-HEATING
100th CYCLE-HEATING
As
Af
1st CYCLE-HEATING
GENERATED STRESS (MPa)
TEMPERATURE (°C)
300
200
100
0
-100
-200
-300
0
100
200
300
400

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EUROPEAN SEARCH REPORT

Application Number
EP 09 01 5086

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X	WO 97/03215 A1 (ULLAKKO KARI MARTTI [FI]; GAVRILJUK VALENTIN [UA]; YAKOVENKO PETER [UA]) 30 January 1997 (1997-01-30) * page 6, line 14 - page 10, line 14; table I * -----	1-15	
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C22C
C21D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	8 April 2010	González Junquera, J

CATEGORY OF CITED DOCUMENTS

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