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Role of Nickel Content in One-Way and Two-Way Shape Recovery in Binary Ti-Ni Alloys

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Abstract: The shape recovery characteristics of titanium nickelide with an Ni content of 50.0 at % and 50.7 at % were studied in a wide range of structures obtained as a result of cold drawing with an accumulated true strain of $\epsilon = 0.52$ and subsequent annealing in the 250 to 700 °C temperature range. Shape memory effect (SME) inducing was carried out by bending using a non-isothermal loading mode, which made it possible to reveal implementing elastic strain in the equiatomic alloy up to 12% and thereby increase the total shape recovery by a factor of 1.5. The obtained results prove that the Ni content strongly affects the value and specific features of changes of the shape recovery characteristics with loading strain as well as grain/subgrain size. In equiatomic alloy, the total recovery strain manifests its maximum of 13.5–15% and the recovery strain of 9% at a loading strain range of 12 to 14%. In Ni-rich alloy, the total recovery strain manifests its maximum of 20% and the recovery strain of 14% at a loading strain range of 15 to 21%. The maximum two-way SME value correlates with the residual strain in both alloys and reaches its maximum of 3.0% in a material with a recrystallized structure. Varying the loading strain value under bending in the 11 to 21% range allows regulation of the temperature of shape recovery in Ni-rich alloy in the 45 to 80 °C range.

Keywords: titanium nickelide; microstructure evolution; softening; martensitic transformations; shape recovery characteristics; comparative study

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1. Introduction

Ti-Ni-based shape memory alloys (SMAs) of near-equiatomic compositions (with Ni content in the range of 0–50.9 at %) remain the most popular as functional materials with a unique set of functional properties. The scope of their application is extremely wide—from intelligent devices for space technologies [1,2] to medical implants [3–5]. In fundamental research and development of various kinds of devices, the attention of scholars and engineers is aimed at ensuring high shape recovery properties: superelasticity (pseudoelasticity), one-way shape memory effect (SME), two-way SME (TWSME), and shape recovery temperatures.

These properties are sensitive to structure, which determines the possibility of using various structural factors for their purposeful control [6–10]. Traditionally, for this purpose, a thermomechanical treatment is used. During post-deformation annealing (PDA), the recovery, polygonization, and recrystallization processes develop. In Ni-rich alloy, these structure changes are accompanied by aging in the 250 to 500 °C temperature range, i.e., precipitation of the Ti_3Ni_4 phase [11,12]. The intensity and completeness of aging in the given temperature range is determined by the temperature and exposure time [13–16]. Structure evolution under aging brings changes in the kinetics, sequence, and staging of martensitic transformations (MT) [17,18], which determine both shape recovery characteristics and the thermomechanical conditions for their implementation [18,19].

To induce SMEs, at least a single deformation is required. Various researchers use various loading modes—bending [20–23], tension [24,25], rolling [26], torsion [27–29], and compression [30,31]—wherein the studied materials are usually limited by a single

alloy of a certain chemical composition. It does not seem possible to compare the shape recovery characteristics obtained under different loading modes and strains as well as under different temperatures because the numerated conditions strongly affect shape recovery values [26,32–34]. To reveal the role of Ni content in Ti-Ni alloys, it is necessary to carry out the systematic comparative studies of at least two alloys—equiatomic and Ni-rich—in a wide range of structures using a similar approach.

The present work focuses on this objective and aims at revealing the effect of Ni content in binary Ti-Ni alloys on one-way and two-way SMEs as well as additional possibilities of their control according to specific task.

2. Materials and Methods

A Ti-50.0 at % Ni alloy was obtained by “MATEK-SMA” (Russia) using vacuum-induction melting furnace (UPPF-3M, Elektromechanika, Rzhev, Russia); a Ti-50.7 at % Ni alloy was smelted using an induction vacuum skull melting furnace. Subsequent redistribution included pressing, rotary forging, hot helical rolling, and warm drawing to obtain a wire with a diameter of 0.58 mm. The final homogenizing annealing was carried out at 700 °C (20 min) with subsequent water quenching. A 0.45 mm diam. wire was obtained by the final cold drawing with a logarithmic area reduction (accumulated true strain) of $\epsilon = \ln(S_0/S_1) = 0.52$ where S_0 and S_1 are the wire cross-section area before and after cold drawing. The heat treatment regimes in the range of 250–700 °C were chosen using data from [9,35,36] to obtain the full spectrum of structures under softening. Structural studies were carried out using a JEM-2100 transmission electron microscope (TEM, JEOL, Tokyo, Japan) operated at 200 kV. Foils were cut off the middle of the wire samples using a scanning ion microscope “Strata FIB 205” (FEI Company, Hillsboro, OR, USA) by local precision ion etching, with the accelerating voltage of a focused ion beam of 30 kV. Calorimetric studies of the martensitic transformations of a Ni-rich alloy were carried out using a “Perkin Elmer” calorimeter (Perkin Elmer LLC, Waltham, MA, USA) under a heating/cooling rate of 10 °C/min in the range of −150 to 100 °C. The start and finish temperatures of martensitic transformations were determined using the ASTM F2004-05 (2010) standard [37]. The SME inducing was performed by bending using the loop-like wire samples (see Figure 1a) and the mode including the following steps: loading at a peak temperature B2→R transformation, then cooling to a temperature of zero for equiatomic alloy and −196 °C for Ni-rich alloy, and unloading at the same temperature and heating. The corresponding peak temperatures for the equiatomic alloy were determined using the DSC plots presented in [9]. The samples were deformed using the cylindrical mandrels of different diameters equipped with a hook (Figure 1a) to fix the loop of the sample. The diameter of the arc formed by the sample at different stages of the experiment was measured using a template with a set of arcs of different diameters [19]. Figure 1a shows the loading procedure and Figure 1b—a typical bending scheme with shape recovery characteristics. The loading strain (ϵ_f) was varied in the range of 10–21%. After unloading, the samples of the equiatomic alloy were gradually heated to 100 and 200 °C; the samples of Ni-rich alloy were heated to 100 °C.

Figure 1. Shape memory effect (SME) inducing and measurements of shape recovery parameters: (a) Deformation of the sample on the mandrel; (b) schematic representation of shape recovery process after bending with the designation of the determined parameters ($R = D/2$, see Formula (1); 1–2 loading; 2–2 cooling under loading; 2–3 elastic recovery strain; 3–4 shape recovery process under heating; 4–5 two-way SME (TWSME) under cooling; adapted from [19]).

The loading strain ε_t (see Figure 1b) was determined as

$$\varepsilon_t = \frac{d}{D + d} \quad (1)$$

where d —the wire diameter, mm; D —diameter of the mandrel used to deform the sample, mm (Figure 1b indicates the radius of the mandrel (R)).

Total recovery strain includes the recovery strain (ε_r) and the elastic strain (ε_{el}):

$$\varepsilon_r^{tot} = \varepsilon_r + \varepsilon_{el}. \quad (2)$$

The formulas for the shape recovery values and their interrelations are given in [19].

3. Results

Varying the time and temperature of annealing after cold deformation, a full spectrum of structures of titanium nickelide under softening was obtained. As a result of cold drawing with an accumulated strain of $\varepsilon = 0.52$, a developed dislocation substructure of B2 austenite with partial amorphization is formed in both alloys (Figure 2a). The structure evolution and DSC plots for Ni-rich alloy are presented in Figures 2 and 3 respectively; similar studies of the equiatomic alloy were performed in [9].

Figure 2. Microstructure (TEM) of Ti-50.7 at % Ni alloy after drawing ($\varepsilon = 0.52$) and post-deformation annealing: (a) As-received after drawing; (b) 500 °C, 0.5 h; (c) 600 °C, 0.5 h; (d) 650 °C, 0.5 h.

Figure 3. Grain/subgrain growth as a result of post-deformation annealing (the curve for equiatomic alloy was plotted using the data of [9]).

PDA at 350 °C is accompanied by recovery and initial polygonization. As a result of aging at 430 °C, a mixed nanostructure of B2 austenite is observed; it consists of subgrains (formed in the areas with the well-developed dislocation substructure) and crystallized grains (formed in the amorphous areas); the average size of structure elements does not exceed 20 nm. After aging at 500 °C, the suppressing part of the volume is occupied by the recrystallized grains; the average size of microstructure elements increases to 80–120 nm

(Figure 2b). After aging in the range of 350–500 °C, the Ti_3Ni_4 precipitates cannot be traced visually but can be interpreted using selected area electron diffraction (SAED) [35,38] and X-ray analysis [39]. Annealing at 600 °C leads to the completion of recrystallization, the grain size is 1.3–1.8 μm after exposure for 0.5 h and 3–4 μm after exposure for 1 h (Figure 2d). An increase in the annealing temperature up to 700 °C (0.5 h) is accompanied by an increase in the grain size to 7–9 microns [18].

The similar structure evolution was found in equiatomic alloy [9] with transition from one structure type to another at 100–150 °C lower temperatures. To compare the grain/subgrain size growth versus temperature grain/subgrain, the corresponding plots are given in Figure 3.

The DSC results shown in Figure 4 permit tracing the evolution of martensitic transformations in the development of softening.

Figure 4. DSC curves of the Ti-50.7 at % Ni alloy after various post-deformation annealings (only the temperature range is shown where martensitic transformations were recorded).

After annealing at 350 °C, at the initial stage of softening, all martensitic transformations are suppressed. Aging at 430 °C brings the appearance of a direct $\text{B2} \rightarrow \text{R}$ transformation at a temperature of 32 °C and a reverse $\text{R} \rightarrow \text{B2}$ transformation at a temperature of 34 °C. The growth of microstructure elements up to 80–120 nm (annealing at 500 °C) shifts a temperature of $\text{B2} \rightarrow \text{R}$ transformation down to 10 °C. The formation of $\text{B19}'$ martensite remains suppressed down to minus 100 °C and becomes possible only upon completion of the recrystallization processes at 600 °C for 0.5 h, when the average grain size reaches 1.3–1.8 μm . In this case, the peak of $\text{B2} \rightarrow \text{R}$ transformation shifts to minus 18 °C. An increase in the annealing time to 1 h at the same temperature of 600 °C (the average grain size is 3–4 μm) brings peaks convergence and after PDA at 700 °C (average grain size 9–11 μm) transition to a one-stage transformation $\text{B2} \rightarrow \text{B19}'$. The reverse martensitic transformation remains one stage in all cases: it corresponds to $\text{R} \rightarrow \text{B2}$ in the range of 430–500 °C and $\text{B2} \rightarrow (\text{R}) \rightarrow \text{B19}'$ in the range of 600–700 °C.

SME inducing (loading) temperatures for each structural state were determined from the position of the $\text{B2} \rightarrow \text{R}$ peak; they are presented in Table 1. Since all martensitic trans-

formations are suppressed after annealing at 350 °C, it is not possible to determine the SME inducing (i.e., loading) temperature. Therefore, taking into account the peak displacement trend toward low temperatures during the development of softening processes (see Figure 4), a deformation temperature of 50 °C was chosen.

Table 1. Loading temperatures for each structure state (correspond to the peak of the B2→R transformation).

Ti-50.0 at % Ni, Determined from [39]						
PDA regimes	250 °C, 1 h	300 °C, 1 h	350 °C, 1 h	450 °C, 0.5 h	500 °C, 1 h	700 °C, 0.5 h
Position of B2→R peak, °C	50	45	45	45	42	40 *
Ti-50.7 at % Ni						
PDA regimes	350 °C, 0.5 h	430 °C, 0.5 h	500 °C, 0.5 h	600 °C, 0.5 h	650 °C, 0.5 h	700 °C, 0.5 h
Position of B2→R peak, °C	50	32	10	−18	−18	−21 *

*—In the absence of B2→R transformation, the loading temperature corresponds to the onset of the martensitic transformation B2→(R)→B19'.

Figure 5 presents the selected results of the shape recovery characteristics of both alloys with a mixed nanostructure (see Figure 5a,c) and a recrystallized structure of B2-austenite (see Figure 5c,d) vs. loading strain. The similar studies were carried out after annealing in all temperature ranges. Although the corresponding plots are omitted in Figure 5, the obtained data are presented in Figures 6 and 7.

Figure 5. Shape recovery parameters vs. loading strain plots of Ti-50.0 at % Ni (a,b) and Ti-50.7 at % Ni (c,d) alloys with a mixed nanostructure (a,c) and recrystallized structure (b,d) after post-deformation annealings: (a) 350 °C, 1 h; (b) 500 °C, 1 h; (c) 500 °C, 0.5 h; (d) 600 °C, 0.5 h.

Figure 6. Shape recovery parameters vs. grain/subgrain size plots of equiatomic alloy in the $\varepsilon_t = 12\text{--}14\%$ range after heating up to (a) $100\text{ }^{\circ}\text{C}$ and (b) $200\text{ }^{\circ}\text{C}$. The range of grain/subgrain size corresponding to the maximum values of ε_r and $\varepsilon_r^{\text{tot}}$ is marked by shading.

Figure 7. Shape recovery parameters vs. grain/subgrain size plots of Ni-rich alloy in the ranges of loading strain: (a) $15\text{--}16\%$; (b) $19\text{--}20\%$. The range of grain/subgrain size corresponding to the maximum values of ε_r and $\varepsilon_r^{\text{tot}}$ is marked by shading.

In all cases, an equiatomic alloy manifests an extreme character in the recovery strain evolution with a maximum in a range of loading strain of $12\text{--}14\%$ (see Figure 5a,b). The recovery strain value manifests its maximum of 9% in a nanostructured material (see Figure 5a) and decreases to 6% in a recrystallized one (see Figure 5b).

In Ni-rich alloy, the recovery strain manifests a parabolic dependence with a maximum value of 14% in a range of loading strain of $10\text{--}21\%$. The ε_r value does not exceed 10% in a nanostructured alloy (see Figure 5c) and reaches 14% in a fine-grained ($\approx 3\text{ }\mu\text{m}$) recrystallized alloy (see Figure 5d).

The total recovery strain $\varepsilon_r^{\text{tot}}$ includes as well the elastic strain, changes in direct ratio in both alloys with a mixed nanostructure, and parabolic dependence in the case of a fine-grained recrystallized structure. It reaches 15% and 20% respectively in an equiatomic alloy and an Ni-rich one. The TWSME value in the presented plots does not exceed 2% .

Note that the shape recovery value as well as the position of its maximum under heating differs in the studied alloys: in the equiatomic alloy, it corresponds to the range of $\varepsilon_t = 12\text{--}14\%$ (see Figure 5a,b), and $\varepsilon_t = 15\text{--}21\%$ for the Ni-rich alloy (see Figure 5c,d).

The loading strain strongly affects the shape recovery temperatures of Ni-rich alloy: the increase from 45 to $80\text{ }^{\circ}\text{C}$ correlates with the increase of loading strain in the range of $11\text{--}21\%$.

Figure 6 presents the diagrams of shape recovery values vs. grain/subgrain size of an equiatomic alloy after SME inducing, subsequent unloading, and heating up to $100\text{ }^{\circ}\text{C}$ (see Figure 6a) and $200\text{ }^{\circ}\text{C}$ (see Figure 6b). The diagrams were plotted using shape recovery

values obtained in the range of loading strain of 12–14%. The value of the elastic strain ε_{el} is marked by an arrow.

After unloading and heating up to 100 °C, the recovery strain maximum $\varepsilon_r = 8 \pm 0.5\%$ is realized in the range of grain/subgrain size 0.07–2.3 μm (see Figure 6a), and the total recovery strain manifests its maximum $\varepsilon_r^{tot} = 13.5 \pm 0.7\%$ in the range of 0.03–0.6 μm . This range is characterized by the maximum contribution of the elastic strain.

The grain/subgrain refinement lower than 0.03 μm as well as the development of recrystallization brings degradation of the recovery strain ε_r ; the total recovery strain ε_r^{tot} decreases only with the recrystallized grain growth.

The residual strain ε_f remains minimal in the range of ultra-fine-grained substructure and gradually increases with the growth of the grain/subgrain size. The TWSME value correlates with the residual strain in the range of 0.2–6.0 μm of the structure elements, reaches its maximum 2.5% in the range of 1.5–2.5 μm , and then decreases.

After unloading and heating up to 200 °C, the recovery strain increases up to $9 \pm 0.5\%$. The value of ε_r^{tot} increases in the material with the recrystallized structure by 2–4% (see Figure 5b). The TWSME value decreases, and the residual strain does not change.

For similar diagrams of Ni-rich alloy, two ranges of loading strain were chosen: 15–16% and 19–20%. The recovery strain manifests an extreme character of evolution with a maximum of $15 \pm 0.5\%$ in the narrow range of the 2–5 μm of the fine-grained recrystallized structure. At that, the total recovery strain ε_r^{tot} manifests a stable plateau at $\varepsilon_r = 13.5 \pm 0.5\%$ in a wide “structure range” of 0.07–5.0 μm (see Figure 7a); the grain growth up to 9–11 μm brings their expressed degradation.

The residual strain ε_f does not exceed 0.2% up to a grain/subgrain size of 0.1 μm and approaches 5% in the range of existence of the recrystallized structure with the grain size of 7–9 μm . The TWSME value gradually increases from 1% in the material with the finest mixed nanostructure to 2.6% with the development of recrystallization.

The increase of the loading strain up to 19–20% (Figure 7b) brings the increase of the total recovery strain ε_r^{tot} up to 20% (which almost coincides with the loading strain) in the narrow range of 0.05–0.2 μm . The ε_r value remains the same, and its “structure range” somewhat expands to 1–6 μm . The TWSME maximum of 3% correlates with that of the residual strain of 5%.

4. Discussion

The described regularities prove that the Ni content in binary titanium nickelide strongly affects the value and specific features of the shape recovery characteristics. The range of their maximum realization is $\varepsilon_t = 12$ –14% for the equiatomic alloy (see Figure 5a,b) and $\varepsilon_t = 15$ –21% for Ni-rich alloy (see Figure 5c,d). The maximum recovery strain ε_r in equiatomic alloy does not exceed 9%; in Ni-rich alloy, it reaches 14%. The maximum total recovery strain ε_r reaches 15%, in equiatomic alloy and 20% in Ni-rich one (see Figures 5–7). A comparative analysis makes it possible to explain the difference between the observed regularities in the functional behavior of alloys with different Ni content.

Under non-isothermal annealing in an equiatomic alloy, only softening processes occur; in Ni-rich alloys during annealing, softening and aging (with precipitation of the Ti_3Ni_4 phase) proceed simultaneously; i.e., there is an overlap of “structural” and “morphological” factors (meaning the structure of the matrix and the morphology of precipitates, respectively). Note that the processes of softening develop with the temperature growth, although the aging process develops in the range of 250–500 °C [11,12] with a maximum of 420–440 °C in its intensity and depth [15,40]. Figure 3 shows that all the stages of softening in the temperature range of 350–500 °C in Ni-rich alloy begin at higher temperatures if compared to an equiatomic alloy with the difference range of 100–150 °C. This phenomenon of “delay” is associated with the decorating effect of the Ti_3Ni_4 precipitates along grain boundaries in the Ni-rich alloy during annealing in the temperature range of 350–500 °C, which results in an obstacle to the migration of dislocations, dislocation sub-boundaries, and grain boundaries [9]. On the other hand, the precipitates create an orienting effect, i.e.,

additional powerful fields of internal stresses, which “work” to improve the shape recovery behavior associated with the availability of martensitic transformations; this contribution is most pronounced in the temperature range of 350–500 °C, when the aging processes are most intense.

In Ni-rich alloy, the initial stage of softening (PDA at 350 °C) is characterized by the suppression of all phase transformation (see Figure 4) that is caused by the preservation of high defectiveness of the structure. The development of polygonization and grain/subgrain growth after PDA at 430 °C causes in the appearance of B2→R transformation; its highest temperature is associated with the most intense aging processes [18,35].

A further decline of B2→R transformation is associated with the stabilization of B2 austenite due to a decrease in the structure defectiveness and the development of recrystallization processes. This tendency persists with a further increase in the annealing temperatures and the development of recrystallization.

The suppression of the martensitic transformation R→B19' in the annealing temperature range of 430–500 °C is associated with the formation of a nanostructure [9,35]. These regularities fit into the known data of the evolution of martensitic transformations inherent in aging Ti-Ni-based alloys [9,40,41]. Comparison with the evolution of the martensitic transformations in the equiatomic alloy [9] confirms the “delay” phenomenon in structural evolution mentioned above.

The specific features of structure formation and martensitic transformations described above reflect the shape recovery behavior and the values of the studied parameters. To analyze the nature of this effect, the following considerations should be taken into account. The shape recovery value is determined by the difference between the dislocation (conventional) and the transformation yield stress $\Delta\sigma$ [42]. The higher this difference, the later the irreversible plastic deformation starts under loading. Aging results in an increase of the dislocation yield stress as well as $\Delta\sigma$, which is a value that confidently correlates with the shape recovery values in Ni-rich alloy [19].

It was found in [41] that $\Delta\sigma$ is lower in the equiatomic alloy vs. the Ni-rich one. Therefore, when using the same loading strain, irreversible plastic deformation in an equiatomic alloy starts at lower deformations than in a Ni-rich one. The above arguments confirm that the observed difference in the shape recovery behavior of equiatomic and Ni-rich alloy is logical and regular.

Despite the fact that the high defectiveness of the structure after annealing in the range of 250–350 °C (for equiatomic alloy) and 350–500 °C (for Ni-rich alloy) causes the suppression of the R→B19' transformation (see Figure 4), the relatively high values of the recovery strain of both alloys indicate that the realization of martensitic transformations becomes possible under load (see Figures 5–7).

In all works devoted to the shape recovery study of an equiatomic alloy from [8] to [43], it was shown that the maximum recovery strain does not exceed 8%, and the elastic recovery strain is near zero. The use of a non-isothermal loading mode in the present study makes it possible to realize relatively high values of the elastic strain (up to 5–8%) and thereby to increase the total recovery strain up to 13–15%. The shape recovery nature when using the mentioned mode is explained in [20]: it is caused by stabilization of the stress-induced martensite under cooling in a loaded condition. The contribution of the elastic strain in shape recovery is maximal in a fine grained/subgrained material and degrades due to recrystallization. Note that the ε_r^{tot} value exceeds the crystallographic resource of the lattice deformation of an equiatomic alloy by 1.5 times. The grain/subgrain refinement lower than 0.07 μm causes the degradation of the recovery stress due to the suppression of martensitic transformation R→B19'; the grain growth brings the degradation of the recovery stress due to decrease of the $\Delta\sigma$ value.

The described correlation between the TWSME value (ε_{TW}) and the residual strain (ε_f) in the equiatomic alloy after subsequent heating up to 100 °C and then 200 °C testifies to the role of the residual stress in realization of the TWSME value. To achieve the maximum

value of the TWSME value, heating to lower temperatures (up to 100 °C) is preferable, at which point the process of relaxation of residual stresses has not yet developed.

The obtained results can be used as an additional approach for the precise regulation of the shape recovery properties in Ti-Ni-based alloys.

As a result of the systematic comparative study of structure evolution, martensitic transformations, and shape recovery characteristics of titanium nickelide with the nickel content of 50.0 at % and 50.7 at %, the following conclusions are formulated.

5. Conclusions

1. The Ni content in a binary titanium nickelide strongly affects the value and specific features of the shape recovery characteristics:
 - The equiatomic alloy manifests its maximum values at 12 to 14% of the loading strain range, while the Ni-rich alloy manifests its maximum values in the 15 to 21% range;
 - In equiatomic alloy, the total recovery strain manifests its maximum of 13.5 to 15% in the range of grain/subgrain sizes of 0.03–0.6 μm and the recovery strain manifests its maximum of 9% in the grain/subgrain size range of 0.2 to 3 μm ;
 - In Ni-rich alloy, the total recovery strain manifests its maximum of 20% in the range of grain/subgrain sizes of 0.05 to 0.2 μm , and the recovery strain manifests its maximum of 14% in the range of grain/subgrain sizes of 0.2 to 3 μm ;
2. The use of the non-isothermal SME inducing mode made it possible for the first time to reveal the possibility of implementing elastic strain in the equiatomic alloy up to 12% and thereby increase the total shape recovery by 1.5 times. The maximum contribution of the elastic strain in shape recovery in both alloys is realized in a material with the ultra-fine-grained structure with the grain/subgrain size up to 0.5 μm .
3. The maximum TWSME value correlates with the residual strain in both alloys and reaches its maximum of 3.0% in a material with a recrystallized structure.
4. Varying the loading strain value by bending in the 11 to 21% of strain range allows regulation of the temperature of shape recovery in Ni-rich alloy in the 45 to 80 °C range.
5. The revealed regularities can be used as additional tools for the control of shape recovery values in titanium nickelide according to the objectives of its various applications.

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