Nanostructured Titanium Nickelide: Realization of abnormally high recovery strain

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Abstract. The paper focuses on the study of the shape memory effect (SME) and two-way SME (TWSME) in nanostructured Ti-50.7 at.%Ni alloy. Two different types of structure were studied: nano-subgrained structure (annealing after the moderate deformation with true strain \(e = 0.6\)) and nanocrystalline structure (annealing after the severe plastic deformation with true strain \(e = 1.55\)). A homogenizing annealing at 700 °C for 20 minutes served as a reference heat treatment (recrystallized structure of austenite). The SME training procedure was carried out in bending under load using eight various isothermal and non-isothermal modes covering all phase states and their combinations. The maximum recovery strain (\(\varepsilon_r = 14.7\%\)) in Ti−50.7%Ni alloy is provided by the nano-subgrained structure with the grain size ≤ 5 \(\mu\)m obtained as a result of 10 h-aging after deformation with true strain \(e = 0.6\), loading in the R-phase state with subsequent cooling in the loaded condition through R→C19' transformation under loading strain \(\varepsilon_t = 15.7\%\). The maximum TWSME value \(\varepsilon_{tw} = 3.5\%\) is provided by the loading in the R-phase state and further unloading.

1. Introduction

The analysis of published works brings to a conclusion that the shape memory effect (SME) and two-way SME (TWSME) inducing is usually performed at a temperature of liquid nitrogen or at a room temperature ignoring the phase state (which is determined by an alloy composition and pre-history of thermo-mechanical treatment). The published results permit establishing, that the maximum levels of recoverable SME and TWSME strains do not exceed 7.5 and 4 % respectively [1–15].

It was shown in recent works [16 – 17] that the strain-temperature mode for way SME and TWSME inducing strongly affects all functional characteristics and can bring twice as much growth of the recovery strain and TWSME value. In cited works however only two modes were used: (1) the traditional mode including first cooling the sample down to −196°C, at which the martensitic transformation is completed, then loading with the following exposure, and then unloading, i.e deformation of thermally induced martensite, and (2) loading in metastable B2-austenite state, then cooling in a loaded condition to −196°C and unloading (i.e. loading through B2→R→B19′-transformation route). Nevertheless, there are no still published works devoted to systematic study of the initial phase state effect on functional properties. The present works aim at filling a gap in this knowledge.

The observed materials bring to an assumption that the possibilities permitting to operate and to enhance SMEs are not used in a full measure. We suppose that there is an additional resource which consists in joint variation of austenite structure/substructure, and initial phase state (under applied stress) and strain–temperature external loading parameters in the total strain range 12 – 19 %.
The regulation of the thermo-mechanical training parameters, i.e. the initial phase state and external action parameters (loading and unloading temperature, load value, loading time, the number of training cycles) opens additional possibilities in properties control. This is an objective of the present work.

2. Materials and methods

The shape memory aging alloy Ti−50.7 at.%Ni has been studied. The martensitic transformation temperatures after quenching, determined by DSC, are as follows: Ms = −26°C, Mf = −34°C, As = −11°C, Af = −1°C. A low-temperature thermo-mechanical treatment (LTMT) of the initial bar of 2 mm in diameter was performed by the warm wire-drawing in several passes with intermediate annealing at 700°C (15 minutes). The 0.3 mm diameter wire used for the further study was obtained by the cold drawing with the accumulated strain of ε = 44 % (ε = 0.6) (reduction of the cross-section area) in last passes without intermediate annealing. The samples of this wire were subjected to post-deformation annealing (PDA) at 430°C, 10 hr. The homogenizing annealing at 700°C, 20 minutes, followed by water quenching and PDA at 430°C, 10 hr was chosen as a reference heat treatment (RHT). The oxidized surface layer was removed by chemical etching in 1HF + 3HNO3 + 6H2O2 solution.

The structure and substructure was studied using a JEOL 2100 transmission electron microscope with accelerating voltage 200 kV. Thin foils were prepared using ion bombardment technique. Characteristic temperatures were measured with heating−cooling rate of 10°C/min using a "Mettler Toledo" DSC.

The SME/TWSME inducing was performed using the training method of bending the wire samples around cylindrical mandrels of various diameters under various modes, included the following steps (Figure 1):

Mode 1: loading at the temperature Af + 5°C, (initial state metastable B2-austenite), exposure and unloading at the same temperature, then heating.

Mode 2: loading at the temperature Af + 5°C (initial state metastable B2-austenite), exposure and unloading at the same temperature, then cooling to −196°C, then heating.

Mode 3: loading at the temperature Tr (initial state metastable R-martensite), exposure and unloading at the same temperature, then heating.

Mode 4: loading at the temperature Tr (initial state metastable R-martensite), exposure and unloading at the same temperature, then cooling to −196°C then heating.

Mode 5: loading at the temperature −196°C (initial state stable B19′-martensite), exposure and unloading at the same temperature, then heating.

Mode 6: loading at the temperature Af + 5°C (initial state metastable B2-austenite), exposure, then cooling in the constrained state to the temperature Tr, exposure and unloading at the same temperature, then heating.

Mode 7: loading at the temperature Af + 5°C (initial state metastable B2-austenite), exposure, then cooling in the constrained state to the temperature −196°C, exposure and unloading at the same temperature, then heating.

Mode 8: loading at the temperature Tr (initial state metastable R-martensite), exposure, then cooling in the constrained state to the temperature −196°C, exposure and unloading at the same temperature, then heating.
Figure 1. Training modes: 1 – 5, isothermal; 6 – 8, non-isothermal: dentated line designates loading process; doubled line designates exposure under loading; single line designates cooling/heating/exposure after unloading

The exposure time under loading was 30 seconds. In all cases the TWSME recovery strain value ($\varepsilon_{TW}$) was measured at a temperature $-196^\circ$C; the last heating was performed to the temperature when shape recovery is completed.

The constraining temperatures for each structural state were chosen based on DSC results. The total strain of external layer under load varied from 12 to 19%.

The induced strain $\varepsilon_i$ was determined at a constraining temperature after unloading (Figure 2). The residual strain $\varepsilon_f$ was determined after unloading and then heating above $A_f$ temperature. The recovery strain $\varepsilon_r$ was determined as the difference between $\varepsilon_i$ and residual strain $\varepsilon_f$. The elastic recovery strain $\varepsilon_{el}$ was determined as the difference between $\varepsilon_t$ (total strain) and $\varepsilon_i$. Note that a possible contribution of superelastic (pseudo elastic) recovery cannot be separated from the true elastic recovery in this experiment. Thus, $\varepsilon_{el}$ is an apparent elastic strain in fact.

Figure 2. Main parameters of shape recovery in bending: $\varepsilon_i$ – induced strain; $\varepsilon_r$ – recovery strain; $\varepsilon_f$ – residual strain; $\varepsilon_{el}$ – elastic recovery strain [18]
All mentioned parameters were determined as

\[ \varepsilon = \frac{d}{(D + d)} \times 100\% \]  

(1),

where \( d \) is the wire diameter, and \( D \) is the diameter of the mandrel (for calculation of total strain) or the diameter of the arc formed by a sample.

3. Results and Discussion

In Figure 3 TEM bright- and dark-field images and selected area diffraction patterns are presented. After thermo mechanical processing (\( e = 0.6 + \text{PDA} = 430^\circ\text{C}, 10\) hr) a mixed nano-subgrained plus nanocrystalline structure is observed. In the dark-field image, the areas consisting of individual nanocrystals alternate with submicron-sized conglomerates of subgrains. The average size of structure elements evaluated from bright field images is about 90 nm. Spotted diffraction rings and azimuthally broadened diffraction spots, reflect high-angle as well as low-angle misorientations of structure elements across the selected area, respectively [19].

RHT at 700\(^\circ\text{C}\) results in formation of the recrystallized austenite structure with average grain size about 11 \( \mu \)m (not shown).

Figure 3. Transmission electron microscopy of Ti–50.7 at%Ni alloy subjected to cold drawing \( e = 0.6 \) and post-deformation annealing at 430\(^\circ\text{C} \), 10 hr; a – bright field image, b – dark field image, c – SAED.

Figure 4 illustrates DSC plots after performed treatments. The austenite dislocation substructure and precipitation solution of \( \text{Ti}_3\text{Ni}_4 \) particles strongly affects temperatures of the direct and reverse martensitic transformations. LTMT (\( e = 0.6 \)) and PDA at 430\(^\circ\text{C} \), 10 hr result in forming a well-developed dislocation substructure of austenite. In this case only B2→R– transformation is distinctly visible under cooling down to \(-70^\circ\text{C}\), while two transformations under heating (Figure 4 a). It means that R→B19’ – transformation range is extended and thus it is not clearly visible in the DSC curve. Two peaks in the heating curve correspond to B19’→R and R→B2– transformations respectively.
In the case of recrystallized austenite (RHT at 700 °C), the single-stage transformation B2→B19' under cooling and B19'→B2 under heating are observed; transformation hysteresis is about 30 °C. Additional annealing at 430°C, 10 hr brings the growth of Ti3Ni4 crystals of and therefore depletion of the solid solution with Ni, which in its turn brings changes in DSC plots. Under cooling, three peaks of B2→R; B2→B19' and R→B19' transformations are observed. Two peaks in the heating curve can be can be explained by B19'→B2–transformation separation in two stages, which is caused by lamination of the solid solution with Ni. Another possible reason for the DSC peak “splitting” can be successive R→B2 and B19'→B2 transformations. Temperatures of the direct and reverse martensitic transformations in Ti–50.7 at%Ni after LTMT are presented in Table 1.

![Figure 4. DSC plots of Ti–50.7 at%Ni after LTMT e = 0.6 and heat treatment (a) 430°C, 10 hr; (b) 700°C, 20 min; (c) 700°C, 20 min + 430°C, 10 hr](image)

Table 1

| Heat treatment after LTMT | Direct transformation | Reverse transformation |
|---------------------------|-----------------------|-----------------------|
|                           | Degree Celsius        |                       |
|                           | $R_s$ | $R_f$ | $M_s$ | $M_f$ | $M_s$ | $M_f$ | $R_s$ | $R_f$ | $A_s$ | $A_f$ | $A_s$ | $A_f$ |
| B2 → R                    | 41    | 35    |      |      |      |      | 10    | 40    | 40    | 45    |      |      |
| R → B19'                  |       |       |      |      |      |      | 40    | 45    | 40    | 49    | 50    | 59    |
| B19'→R                    |       |       |      |      |      |      |       |       |       |       |       |       |
| B19'→B2                   |       |       |      |      |      |      |       |       |       |       |       |       |
| B19'→B2                   |       |       |      |      |      |      |       |       |       |       |       |       |
| 430°C, 10 hr              | 47    | 37    |      |      |      |      | 42    | 37    | 42    | 37    |      |      |
| 700°C, 20 min + 430°C, 10 hr | 47    | 37    | $-1$ (R→B19') |      |      |      |      |       | 18    | $-1$ (R→B19') | 49    | 50    | 59    |

The loading temperatures for each structural state were chosen based on DSC results.
The level of the functional properties (FP) and the character of their evolution vs total (loading) strain strongly depend on the alloy structure and the initial phase state: Figures 5 and 6 illustrate their regularities.

After LTMT and PDA at 430°C, 10 hr (mixed nano-subgrained plus nanocrystalline structure), when using isothermal Modes 1 and 2 the elastic strain, the recovery strain and TWSME values manifest more or less pronounced extremum under the total strain 16%. The apparent elastic strain maximum is about 14%, the SME recovery strain maximum does not exceed 1.5%; the TWSME recovery strain value manifests 2.3%. The residual strain grows from 0.4% at $\varepsilon_t = 12\%$ to 11% at $\varepsilon_t = 19\%$.

Change to Mode 3 and 4 brings the elastic strain degradation and growth of the SME recovery strain and TWSME value in all range of total strains: $\varepsilon_{el}$ maximum drops to 10%, $\varepsilon_r$ maximum grows up to 4.5% (Mode 3) and 5.5% (Mode 4), TWSME value -- up to 3.5% (Mode 3) and 3% (Mode 4). The residual strain grows to $1 - 1.5\%$ (at $\varepsilon_t = 11 - 16\%)$ and does not change at $\varepsilon_t = 19\%$ (if compared with Modes 1–2).

![Figure 5](image_url)

**Figure 5.** Evolution of SME and TWSME parameters of Ti–50.7 at.%Ni alloy after LTMT, $e = 0.6$ plus PDA at temperature 430°C, 10 hr under various training Modes. The 1st, 2nd and 3rd columns for each parameter correspond to $\varepsilon_t = 12$, 16 and 19%, respectively.

Transition to Mode 5 brings changes in described regularities: the elastic strain gradually grows from 5 to 10% with total strain growth, the SME recovery strain manifests its maximum $\varepsilon_r = 7\%$.
at $\varepsilon_t = 16\%$ and does not drop below 6.5% in the whole range. TWSME value somewhat decreases to 1.5% at $\varepsilon_t = 12$–16% (if compared with Modes 3–4) and reaches its maximum 2.5% at $\varepsilon_t = 19\%$. The residual strain maximum drops from 11% (Mode 3) to 2.5%.

All described results were obtained under training using isothermal modes. Change to non-isothermal modes brings pronounced changes in evolution and level of all measured parameters. Temperature training regimes of Mode 6 could be logically compared with that of Modes 1–5.

Cooling in a loaded condition from 50 to 40 °C (through B2→R transformation) brings the elastic strain degradation: its maximum at $\varepsilon_t = 16\%$ compounds 8%. The recovery strain maximum keeps the same value as if using Mode 3, but in the rest range it grows. At the same time TWSME value drops in the whole range; the residual strain maximum drops to 8.5%.

The described tendency is much more pronounced in Mode 7 (cooling through B2→R→B19′–transformation) and Mode 8 (cooling through R→B19′–transformation). The elastic strain maximum drops to 3.5% (Mode 7) and to 1% (Mode 8), the recovery strain maximum grows to 12% (Mode 7) and to 14.7% (Mode 8). TWSME value does not exceed 2.5% in both cases. The residual strain maximum drops to 9.5% (Mode 7) to 5% (Mode 8).

It is important to note here that the abnormally high value $\varepsilon_r = 14.7\%$ in Ti–50.7 at.%Ni alloy exceeds the theoretical (crystallographic) resource of the martensitic transformation lattice strain, which amounts to about 10.5% for the studied alloy composition [20].

The structural mechanisms of the above described abnormally high strain recovery need a special study, however, we would like to note that the analogous results were obtained in [21] for single crystals in the same alloy and explained by the effect of additional special twinning on $\{113\}_{B19}$ planes. Another hypothesis on the mechanism of additional recovery strain is additional martensitic transformation, which develops after the crystallographic resource of B2→R→B19′–transformation is exhausted [16, 17]. The observed effects could be also explained by a dynamic model of supersonic martensitic crystal growth [22]. Note that abnormally high recovery strain can be realized as a summary contribution of the shape memory effect and superelasticity.

Figure 6 illustrates evolution of the FP of the alloy with recrystallized structure (RHT at 700°C) vs total (loading) strain.

Using isothermal Modes 1 and 2 bring practically identical results: the elastic strain, the recovery strain and TWSME value manifest slightly pronounced extremum under total strain 16%. The elastic strain maximum compounds ~7% (which is twice lower than in the mixed nanostructure); the recovery strain maximum compounds 4.5% (3 times higher than in the mixed nanostructure); the TWSME value manifests 2.5% (the same as in mixed nanostructure). The residual strain grows from 1.5% (at $\varepsilon_t = 12\%$) to 8.5% (at $\varepsilon_t = 19\%$).

Change to Mode 3 and 4 does not bring evident changes in the elastic strain evolution (if compared with Modes 1, 2). At the same time the recovery strain manifests its maximum ~6% under $\varepsilon_t = 16\%$ and then gradually drops. The TWSME value grows up to 3.5% and the residual strain ~ up to 7–8% (at $\varepsilon_t = 19\%$ both).

Transition to Mode 5 brings changes in the material behaviour: it fails at $\varepsilon_t = 19\%$. The elastic strain grows from 4% to 7% in the range 11–16% of the total strain, the recovery strain manifests its maximum $\varepsilon_r = 7.5\%$ at $\varepsilon_t = 16\%$, TWSME value somewhat drops to 1–2% at $\varepsilon_t = 12$–16% (if compared with Modes 3–4) and the residual strain maximum drops to 0.5%.

Change to non-isothermal Mode 6 does not bring pronounced changes in evolution and level of all measured parameters (if compared with Mode 4). The elastic strain keeps the same value in the whole range of total strain (if compared with Mode 4); the recovery strain does not
practically change and keeps the level of 5.5%; TWSME value drops to 1.5 – 2% and the residual strain maximum does not exceed 6.5%.

Using Mode 7 (cooling through B2→R→B19′-transformation) and 8 (cooling through R→B19′-transformation) brings pronounced changes in evolution of measured parameters. The elastic strain maximum drops to 1% in both cases, the recovery strain maximum reaches its maximum 11% (Mode 7) and to 10.5% (Mode 8). TWSME value maximum reaches 3.2% (Mode 7) and 2% (Mode 8). The residual strain maximum reaches 11% (Mode 7) and 10% (Mode 8).

The conducted experiments permit realising the abnormally high recovery strain of SME in Ti–50.7 at.%Ni alloy: $\varepsilon_r = 14.7\%$ provides mixed nano-subgrain and nanocrystalline structure after LTMT and PDA 430°C, 10 hr under loading through R→B19′-transformation with $\varepsilon_t = 16\%$. The TWSME maximum $\varepsilon_{TW} = 3.5\%$ after loading with $\varepsilon_t = 16\%$ provides the mixed structure and training in metastable R-martensite state with total strain 16.0% and then heating; the same TWSME value corresponds to the recrystallized structure after annealing at 700°C, 20 minutes and training through B2→R→B19′-transformation with the total strain 14%.

The described results seem to be perfectly regular; SME and TWSME parameters are strongly dependent upon structure, initial phase state and deformation method.

Figure 6. Evolution of SME and TWSME parameters in Ti–50.7 at.%Ni alloy after RHT at a temperature 700°C, 20 min and heat treatment 430°C, 10 hr under various training Modes. The 1st, 2nd and 3rd columns for each parameter correspond to $\varepsilon_t = 12$, 16 and 19%.
The diagrams in Figures 5, 6 permit analyzing the obtained regularities and allocating the zones of paramount influence of various factors, affecting functional parameters when training using various initial phase states.

But for all that we must bear in mind the circumstances as follows:

1) the elastic recovery strain cannot be separated from the superelastic recovery in the used experimental method. Therefore, the measured $\varepsilon_r$ which describes only SME recovery strain may not be a full measure of the recoverable strain after the certain treatment, because of a possible contribution of the superelastic recovery;

2) the shape recovery ability is evaluated as a sum of the recovery strain due to SME and superelasticity, i.e. $\varepsilon_r + \varepsilon_{rs}$. Since we cannot pick out $\varepsilon_{rs}$ of $\varepsilon_{el}$, the shape recovery ability must be evaluated as a total recovery strain:

$$\varepsilon_{rtot} = \varepsilon_r - \varepsilon_f$$

Nevertheless, the measured parameters $\varepsilon_r$ and $\varepsilon_i$ do not lose their importance, because they characterize shape recovery due to SME, whereas TWSME value indirectly points to cold-work strengthening and/or ageing.

When training in $\beta_2$–austenite (Modes 1, 2) the effect of cooling/heating after unloading is not practically pronounced: all measured parameters change insignificantly (cooling or heating after unloading do not strongly affect the parameter value). This is evenly for both mixed and recrystallized austenite structure.

After LTMT and PDA 430°C, 10 hr (the mixed structure), $\beta_2$–austenite is metastable at a loading temperature. On reaching the transformation yield stress, $\beta_2$–austenite transforms to oriented stress-induced martensite. When unloading, the martensite re-orientates back to austenite by a superelastic recovery mechanism. Therefore the material manifests high level of the elastic recovery strain in this range of the total strains $\varepsilon_t = 12 – 16\%$. When $\varepsilon_r$ reaches 19%, the elastic recovery strain drops significantly being accompanied by the residual strain growth (see Fig.5). Such pronounced changes are caused by reaching and exceeding the dislocation yield stress of austenite and as a consequence, triggering plastic deformation of austenite and perhaps of martensite (which is justified indirectly by the presence of TWSME). In that case $\varepsilon_{el}$ degradation and $\varepsilon_{f}$ growth seem to be perfectly regular.

The described regularities are equitable for training started from R-martensite state (Modes 3, 4). In that case R-martensite is stable at a loading temperature and the strain accumulates due to R-phase re-orientation and then oriented $\beta_1\sigma'$–martensite formation. In the range of $\varepsilon_t = 12 – 16\%$ the elastic recovery strain remains significant, but manifests the lower level than in the case of $\beta_2$-austenite loading. However the induced strain (it is not presented in Figs. 5, 6) is somewhat higher. We can suppose that this is caused by the residual stress both in R–phase and stress-induced $\beta_1\sigma'$–martensite, because the loading temperature is lower than $A_t$ and the stress-induced martensite is stable after unloading. It is important to note here that TWSME value manifests its maximum 3.5% when using R-phase training with further cooling and corresponds to the mixed structure.

At a temperature $-196^\circ$C, the stable phase is $\beta_1\sigma'$–martensite (thermally induced martensite). The strain under loading accumulates due to its re-orientation and further plastic deformation (the latter is confirmed by residual strain growth) and, as we suppose, additional martensitic transformation, which develops after the resource of $\beta_2\rightarrow R\rightarrow \beta_1\sigma'$-transformation is exhausted. Its contribution grows under further increase of $\varepsilon_t$ and the elastic recovery manifests the parallel
growth. Superelasticity is partially realized due to reverse reorientation of stress-induced martensite and oriented additional martensite, which determines the elastic recovery strain value. When change to B2→R–transformation (Mode 6), the above described processes remain the same as training from B2 (Modes 1, 2) and R–phase (Modes 3, 4) states. The stress-induced martensite remains stable under unloading.

Change to non-isothermal scheme brings pronounced changes in evolution of measured parameters.

When cooling through B2→R→B19’–transformation in a loaded condition (Mode 7) and then unloading at −196°C, the strain accumulates due to orientation of R-phase, formation of oriented stress-induced martensite, and oriented additional martensite (which is indirectly verified by pronounced strain recovery growth). At unloading temperature the oriented cooling-induced martensite and stress-induced martensite are stable. The elastic strain degradation in this case is pronounced significantly and keeps practically the same level in the whole range of the total strain. The recovery strain manifests the pronounced maximum 12% at εt = 16%. Its growth in the range of εt = 11 – 16% is due to growing martensite stabilization; its further degradation at εt = 18% is caused by development of plastic deformation (which is verified by the residual strain growth).

The described regularities keep the same when using loading through R→B19’–transformation (Mode 8). The strain accumulates due to reorientation of R-phase, formation of oriented stress-induced martensite, and oriented additional martensite (or specific twining). Using this mode brings the recovery strain maximum εr = 14.7 % at εt= 15.7% in the material with the mixed structure. The obtained result leads to a conclusion that the character of generated stress in that case seems to be most favorable for realization of the recovery strain maximum.

After RHT at 700°C, when the grain size in the recrystallized structure reaches 11 µm the dislocation yield stress, i.e. involving of plastic flow in the deformation process, becomes the leading factor in FP regulation. The yield stress degradation removes the material from the temperature range of superelastic behavior. At the same time the εs contribution grows. The pronounced weakening at 700°C prevents the manifestation of superelasticity. Finally, this brings the recovery strain degradation to 7 – 11 % and the residual strain growth to 5%.

Analyzing these regularities, they can be classified in three groups of paramount influence of various factors in SME parameters control (in various initial phase states). The first and the second ones are characterized with the high level of the elastic recovery strain εe. The first group includes Modes 1–4 and 6 (see Figure 1): in all these cases the high level of the elastic recovery strain is caused by reverse transformation of stress-induced martensite to austenite. The second group is represented with only Mode 5, where the elastic recovery strain is cased by the reverse re-orientation of the deformed cooling-induced martensite. The third group includes Modes 7 and 8; it is characterized with the pronounced extreme evolution of the recovery strain εr (as a function of the total strain εt). In this group, the εr contribution reaches its maximum and the εel contribution drops to 0.5% (see Figures 5, 6).

The obtained results lead to a conclusion that the character of evolution and realised SME and TWSME values are determined by the alloy structural condition and initial phase state before training procedure. It was shown in [18, 23] that the formation of Ti3Ni4 precipitates, especially as a result of continuous aging in hyper-equiatomic Ti–Ni alloys, introduces the additional contribution to FP formation. It is common knowledge that martensite variants are induced by oriented stresses around coherent Ti3Ni4 precipitates [23, 24] Thus, these precipitates introduce the contribution to internal stresses which are responsible for SME and TWSME realization. Increasing of aging time leads to an increase in the number of these precipitates and then their
growth. As a consequence, the precipitates growth leads to irregularity of their coherent boundaries with the matrix, and concentration changes in the solid solution, which must affect shape memory characteristics.

On the one hand, the precipitates exert orienting effect upon internal stress fields which bring growth of the characteristics dependent upon martensitic transformation process. On the other hand, hypothetically, they decorate subgrain boundaries hindering subgrain growth (which remain in nano-size range) and thereby bring suppression of martensitic transformation and properties degradation.

This contribution is most pronounced after PDA at 430 °C, when aging processes develop most extensively. The presence of nanocrystalline structure intensifies this contribution: in [4] it was shown that nanocrystalline structure brings degradation of the abnormally high SME and TWSME. On the whole, contribution of aging process appear in SME and TWSME growth and provides abnormally high recovery strain [16 – 17]. The high dislocation yield stress after LTMT and PDA at 430°C causes the wide temperature range of superelasticity.

The obtained results lead to a conclusion that SME training started from the mixed structure allows regulating SM and superelasticity effects most effectively. At higher inducing temperatures contribution of the elastic and superelastic strain prevails while at lower temperatures this contribution drops, but SME contribution grows. At the same time, the residual strain keeps the low level until over-deformation occurs.

As a whole, the obtained regularities of the initial phase state effect on SME parameters keep themselves within the knowledge system about mechanisms and methods of SMEs control and define their particular features.

**Conclusions**

1. The initial phase state and grain/subgrain structure of Ti–50.7 at%Ni alloy strongly affects functional properties realized under bending tests.
2. Abnormally high recovery strain ($\varepsilon_r = 14.7\%$) is provided by the mixed (nano-subgrained plus a nanocrystalline structure) obtained as a result of 430°C, 10 hr annealing after LTMT with true strain of 0.6 and training through $R\rightarrow R'\rightarrow C19'$ transformation with total strain of 15.7%.
3. The maximum TWSME value $\varepsilon_{tw} = 3.5\%$ corresponds to the mixed structure and training from metastable $R$-martensite state with total strain 16.0% and then heating; the same TWSME value corresponds to the recrystallized structure after annealing at 700°C, 20 minutes and training through $B2\rightarrow R\rightarrow B19'$–transformation with the total strain of 14%.
4. LTMT allows regulating shape memory and superelasticity effects in a wide range: at higher inducing temperatures contribution of the elastic and superelastic strain prevails while at lower temperatures this contribution drops, but SME contribution grows.

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References

[1] Kovnerysty Yu, Fedotov S, Matlakhova L, Oleynikova S 1986 Shape memory effects and shape recovery in Ti - Ni vs strain. – *Fis. Met. Metalloved.*, vol. 62, issue 2, 1986, pp 344–349 /in Russian/

[2] Zeldovich V, Sobyanina G, Rinkevich O 1996 Influence of pre-strain on shape memory effects and martensitic structure in titanium nickelide. Dilitometric effects of martensitic transformations. – *Fis. Met. Metalloved.*, vol 81, issue 3, 1996, pp 107–116 /in Russian/

[3] Liu Y, Liu Y, Van Humbeeck J. Two-way shape memory effect developed by martensite deformation in NiTi. – *Acta mater.* vol 47, Nº.1, 1999, pp 199–209

[4] Antunes A, Tosetti J, Otubo J 2013 High shape recovery Ni–Ti SMA wire produced from electron beam melted ingot. – *Journal of Alloys and Compounds* vol.577S pp 265-267

[5] Wang Z, Zu X, Zu X, Feng X, Dai J 2002 Effect of thermomechanical treatment on the two-way shape memory effect of NiTi alloy spring. – *Materials Letters* 54, 2002, pp 55–61

[6] Saigal A, Fonte M 2011 Solid, shape recovered “bulk” Nitinol: Part I—Tension–compression asymmetry. – *Mat. Sci. Eng.* A 528, 2011, pp. 5536 – 5550

[7] Filip P, K. Mazanec 1966 The two-way memory effect in NiTi alloys. – *Acta Materialia*, vol. 35, Nº. 3, pp 349–354

[8] Undisz A, Fink M, Rettenmayr M 2008 Response of austenite finish temperature and phase transformation characteristics of thin medical-grade Ni–Ti wire to short-time annealing. *Scripta Materialia* vol.59 pp 979–982

[9] Shakeri M S, Khalil-Allafi J, Abbasi-Chianeh V, ArashGhabchi 2009 The influence of Ti3Ni4 precipitates orientation on two-way shape memory effect in a Ni-rich NiTi alloy *Journal of Alloys and Compounds* vol.485 pp 320–323

[10] Li Y F, Mi X J, Tan J, Gao B.D 2009 Thermo-mechanical cyclic transformation behavior of Ti–Ni shape memory alloy wire *Materials Science and Engineering A* vol.509 pp.8–13

[11] Mitwally M E, M. Farag 2009 Effect of cold work and annealing on the structure and characteristics of NiTi alloy Materials Science and Engineering A vol.519 pp 155–166

[12] Balak Z, Abbasi S.M 2011 Influence of the Ti content, training cycles and pre-strain on the two-way shape memory effect in NiTi alloys *Materials and Design* vol.32 pp 3992–3996

[13] Foroozmehr A, Kermanpur A, Ashrafizadeh F, Kabiri Y 2012 Effects of thermo-mechanical parameters on microstructure and mechanical properties of Ti–50 at.%Ni shape memory alloy produced by VAR method *Materials Science and Engineering A* vol.535 pp.164–169

[14] Urbina C, De la Flor S, Ferrando F 2010 R-phase influence on different two-way shape memory training methods in NiTi shape memory alloys *Journal of Alloys and Compounds* vol.490 pp 499–507

[15] Ryklina E P 2013 Influence of Strain–Temperature Training Parameters on shape memory effects in Ti–Ni–based alloys (review) *Proc. 10th International Congress «Machines, Technologies, Materials 2013» XXI* vol 10/147, ISSN 1310-3946, 18–20 September, Varna, Bulgaria, pp 16–20

[16] Ryklina E P, Prokoshkin S D, Chernavina A A 2009 Shape Memory Behavior in Nanostructured Ti–Ni Alloy. *Proc. 8th Int. Symp. ESOMAT 2009* DOI:10.1051/esomat/200905025, pp 1–6

[17] Ryklina E P, Prokoshkin S D, Chernavina A A., Kreytsberg A Yu. Abnormally high shape memory properties in titanium nickelide. *Journal of Alloys and Compounds*, V. 577, Suppl. 1, 15 November 2013, pp. S255-S258
[18] Braïlovski V, Prokoshkin S, Terriault P, Troshu F (Eds.) Shape Memory Alloys: Fundamentals, Modeling and Applications (Montreal: ETS Publ., 2003. 851 p
[19] Prokoshkin S D, Braïlovski V, Korotitskiy A V, Inaekyan K E, and Glezer A M 2010 Specific Features of the Formation of the Microstructure of Titanium Nickelide upon Thermomechanical Treatment Including Cold Plastic Deformation to Degrees from Moderate to Severe The Physics of Metals and Metallography 2010 vol. 110 No. 3 pp 289–303
[20] Prokoshkin S D, Korotitskiy A V, Brailovski V, Inaekyan K E and Dubinskiy S M 2011 Crystal Lattice of Martensite and the Reserve of Recoverable Strain Resource of Thermally and Thermomechanically Treated Ti–Ni Shape Memory Alloys The Physics of Metals and Metallography, vol. 112 No 2 pp 170–187
[21] Chumlyakov Yu, Panchenko E, Kireeva I, Karaman I, Maier H J, Timofeeva E 2013 Shape memory effect and high-temperature superelasticity in high-strength single crystals J. Alloys and Compounds vol 577 ICOMAT suppl 1 pp s393–s398
[22] Kashchenko M P, Chashchina V G 2011 Dynamic model of supersonic martensitic crystal growth Physics – Uspekhi 54(4) 331–349 DOI: 10.3367/UFNe.0181.201104a.0345
[23] Otsuka K and Wayman C M 1998 Shape Memory Materials (Cambridge University Press, United Kingdom. 284 p
[24] Otsuka K, Ren X 2005 Physical metallurgy of Ti–Ni-based shape memory alloys Progress in Materials Science vol.50 pp 511–678