Calculation of hardening contributions of the TiNi alloy undergoing martensitic transformations in a free state

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Abstract. The paper reports on the studies of the effect of thermal cycling on the microstructure of the Ti - 50.8 at. % Ni alloy in coarse-grained and ultrafine-grained states, mechanical properties, and calculation of contributions to hardening in the studied states. The comparison of the calculated and experimental values of the yield stress in the TiNi alloy was carried out.

1. Introduction
The TiNi shape memory alloys are widely used due to their excellent functional properties [1,2]. TiNi alloy products and elements usually undergo a cyclic phase (martensitic) transformation between B2 (A) austenite and B19' (M) martensite during use. Consequently, it can be said that the stability of the phase transformation during multiple transformations is of decisive practical importance. The defects, mainly dislocations, which tend to suppress the martensitic transformation (MT), are introduced during the cyclic thermally induced transformation A→M [3–5]. A shift of the MT temperatures towards lower ones is often observed during thermal cycling [6, 7]. After a certain number of thermal cycles, the transformation behavior can be stabilized by saturating the defects caused by thermal cycling [5].

The design of products with SME imposes certain requirements on the physical, mechanical, and functional properties and their stability. It is possible to additionally improve the properties of shape memory alloys by forming an ultrafine-grained (UFG) state in them by the methods of severe plastic deformation (SPD), in particular, by equal-channel angular pressing (ECAP), by the method of high pressure torsion (HPT), or by a combination of various methods [8-13]. Both deformation and cyclic effects have a significant effect on the microstructure and, accordingly, on the mechanical behavior of the material and on the yield stress $\sigma_{YS}$. To analyze the mechanical properties with different microstructures in alloys, the calculation of the hardening contributions according to the known equations are performed. In particular, the Hall - Petch relationship is used, which is well studied for single-phase and two-phase alloys [14-15], but was little analyzed for materials with different grain sizes that undergo stress-induced martensitic transformation during tensile tests before the onset of plastic deformation. Several studies on alloys undergoing stress induced transformation report on the stress required to trigger the transformation (trigger stress) [16–18]. But it is worth noting that the
stress required for transformation under load is significantly less than the yield stress, and probably should not affect the Hall-Petch relationship.

In this work, the contributions to hardening are considered for the example of the Ti - 50.8 at. % Ni alloy with a high nickel content undergoing cyclic martensitic transformation.

2. Experimental

The material for the study was a binary alloy of the TiNi - Ti - 50.8 at. % Ni. To obtain a solid solution, quenching was carried out from the homogeneity region (heating at a temperature of 800 °C in a Nabertherm muffle furnace for 1 hour) into water. The average grain size of the hardened alloy was about 20 ± 2 microns. An ultrafine-grained (UFG) structure with an average grain size of 350 ± 10 nm was obtained by the ECAP method (USATU equipment) according to the mode - 8 passes, route B, T = 450 °C, the angle of intersection of the channels (φ) - 120 ° [19].

Cyclic martensitic transformations were carried out according to the regime described in [20-22]. X-ray diffraction studies of the samples were carried out on a Rigaku Ultima IV diffractometer (U = 40 kV and I = 35 mA) at room temperature in the angle range 2θ = 30 - 120 °. The dislocation density was calculated by processing the X-ray structural study data using the MatLab software. The study of the microstructure was carried out on a JEOL JEM-2100 transmission microscope, foils for the study were obtained using a Tenupol-5 setup in a solution of 10% perchloric acid and 90% butanol. Mechanical tensile tests were carried out at a strain rate of 10^{-3} s^{-1} at room temperature. In the dislocation theory, the main hardening mechanisms providing an increase in the plastic flow stress are divided into [23]: hardening by dissolved interstitial or substitutional atoms, hardening by dislocations, hardening by grain and subgrain boundaries, hardening by dispersed particles. E. Orowan [24] found that the superposition of each of the hardening mechanisms with the lattice friction stress is linearly additive; the yield point of a hardened material is the sum:

\[ \sigma_{0,2} = \sigma_0 + \Delta\sigma_{s.s.} + \Delta\sigma_{d.p.} + \Delta\sigma_d + \Delta\sigma_g, \]  
(1)

where \( \sigma_0 \) is the frictional stress of the crystal lattice; \( \Delta\sigma_{s.s.} \) - increase in yield strength due to solid solution hardening; \( \Delta\sigma_d \) - increase in the yield strength due to dislocation (strain) hardening; \( \Delta\sigma_g \) is the increase in the yield point due to grain boundary hardening; \( \Delta\sigma_{d.p.} \) - an increase in the yield stress due to precipitation hardening [23].

The frictional stress in the crystal lattice (Peierls-Nabarro stress) is calculated by the formula:

\[ \sigma_0 = \sqrt{2G/(1-\nu)}\exp[-2\pi/(1-\nu)], \]  
(2)

where \( \nu \) is the Poisson's ratio, \( G \) is the shear modulus of the matrix [23].

Solid solution hardening is described by the Mott-Nabarro mechanism according to the formula:

\[ \Delta\sigma_{s.s.} = 2,5Gdelta_L^3/C_L, \]  
(3)

where \( \delta_L \) is the parameter of the dimensional mismatch between the atoms of the dissolved element and the matrix, \( C_L \) is the atomic concentration of the alloying element [23].

Strengthening in the case of incoherent precipitates is described by the Orowan mechanism and is calculated by the formula:

\[ \Delta\sigma_{d.p.} = 0,85Gb/l-D, \]  
(4)

where \( b \) is the Burgers vector, \( l \) is the average distance between the centers of particles, \( D \) is the average size of particles [23].

The qualitative dependence of the plastic flow stress on the dislocation density is described by the following formula:

\[ \Delta\sigma_d = \alpha mGb\sqrt{\rho_d}, \]  
(5)

where \( \alpha \) is the parameter of interdislocation interaction, \( m \) is the orientation coefficient, \( G \) is the shear modulus of the matrix, \( \rho_d \) is the dislocation density [23, 25].

A decrease in the grain size contributes to an increase in the density of grain boundaries in polycrystalline materials, that prevent the development of plastic deformation, since grain boundaries are effective barriers to the movement of dislocations. Grain-boundary hardening is described by the Hall-Petch relationship:
\[ \Delta \sigma_g = k_g d^{-m}, \]  

where \( k_g \) is the coefficient of grain-boundary hardening, \( d \) is the average grain size, \( m \) is the coefficient of the angle of misorientation.

3. Results and discussion

According to the obtained TEM data in the CG state without thermal cycling grain boundaries and triple junctions of grains free from dislocations are observed in the microstructure of the alloy, the average grain size is about 20 ± 5 μm (Figure 1, a). Thermal cycling with the maximum number of heat changes retains the dislocation structure in the form of clusters and disordered walls and dislocation tangles (Figure 1, b). After applying the ECAP method, the transformation of the initial coarse-grained structure into an inhomogeneous grain-subgrain ultrafine-grained structure with an increased density of dislocations is observed (Figure 1, c). As the number of martensitic transformation cycles increases, grains with predominantly nonequilibrium boundaries are observed in the structure, which may indicate a high imperfection of the structure, in the form of an accumulation of dislocations; after the maximum number of thermal changes, it decreases to 260 ± 20 nm (Figure 1, d).

Analysis of the structural parameters showed that in both states there is a decrease in coherent scattering regions (CSR) values, an increase in internal microdistortions, and an increase in the dislocation density associated with them. The increase of the dislocation density in the ultrafine-grained state is higher than in the coarse-grained state, which indicates that a high density of grain boundaries and a smaller grain size contribute to the intensity of defect accumulation.
Table 1.- Parameters of the structure of the Ti - 50.8 at.% Ni alloy in various states

| State     | Parameters of lattice a, Å | CSR, nm | $<\varepsilon^2>^{1/2} \times 10^{-4}$ | $\rho \times 10^{15}$, m$^{-2}$ |
|-----------|---------------------------|---------|-------------------------------------|---------------------------------|
| CG        | 3,013±0,001               | 550     | 0,8                                 | 0,5                             |
| CG+TC     | 2.895±0,001 (monoclinic)  | 320     | 2,2                                 | 1,6                             |
| UFG       | 3,011±0,003               | 170     | 2,7                                 | 5,3                             |
| UFG+TC    | 3,013±0,001               | 120     | 3,4                                 | 7,1                             |

Table 2 shows the data of mechanical tensile tests and calculations of contributions to hardening by formulas (1-6). Since the concentration of alloying elements is exceedingly small, the value of solid solution hardening is equal to 0 MPa, similarly, the value of the contribution from incoherent particles is equal to zero. Therefore, the main contributions to hardening are the Peierls-Nabarro stress, dislocation hardening, and grain-boundary hardening described by the Hall-Petch relationship.

Table 2. Results of mechanical tensile tests of the Ti - 50.8 at.% Ni alloy in various states *

| State     | Ultimate strength $\sigma_{UTS}$, MPa | Calculated yield strength, $\sigma_{YS}$, MPa | Yield strength $\sigma_y$, MPa | Phase yield stress, $\sigma_{ym}$, MPa | Estimated reactive stress $\sigma_r$, MPa | Elongation $\delta$, % | Reversible** deformation $\varepsilon_{rev}$, % |
|-----------|--------------------------------------|---------------------------------------------|-------------------------------|--------------------------------------|----------------------------------------|-----------------------|---------------------------------------------|
| CG        | 940                                  | 5.146                                       | 390.5                         | 292.609                              | 495                                    | 320                   | 175                                         | 50                           | 4,0                             |
| CG+TC     | 1075                                 | 5.146                                       | 166.023                       | 383.614                              | 685                                    | 505                   | 180                                         | 55                           | 5,1                             |
| UFG       | 1155                                 | 5.146                                       | 302.166                       | 526.314                              | 690                                    | 295                   | 340                                         | 30                           | 4,2                             |
| UFG+TC $n=250$ | 1075                                 | 5.146                                       | 349.733                       | 626.439                              | 765                                    | 460                   | 305                                         | 40                           | 5,7                             |

* Errors in determining $\sigma_{YS}$ - ± 5%, $\sigma_{UTS}$ - ± 5%, $\sigma_{ym}$ - ± 5%, $\delta$ - ± 5%, $\varepsilon_{rev}$ - ± 10%

** Estimated - along the length of the plateau at the stage of phase yield stress

The most sensitive characteristic to thermal cycling is the yield stress. In both states of the alloy, it increases with an increase in the number of cycles. The UFG state before TC is characterized by higher values of strength and yield stress due to the contribution of grain boundary hardening. The ultimate strength in the coarse-grained state increases to 150 cycles, then the values decrease. This is probably since after a certain number of cycles (in this state $n = 150$), saturation occurs in the material and no further increase in characteristics is observed. In the UFG state, with an increase in the number of cycles of multiple transformations, the values of the ultimate strength increase to 100 thermal cycles, then a decrease in the parameter is observed, which can be explained by the inhomogeneity of the formed structure.

The greater difference between the calculated value of the yield stress and the results of mechanical tests in states after thermal cycling may be associated with a more complex structure formed during thermal cycling. The differences for the ultrafine-grained state can also be explained by the fact that a
complex defect structure is formed in the samples, which complicates the flow of dislocations during tensile tests.

4. Conclusions
As a result of thermal cycling in the coarse-grained and ultrafine-grained states, an increase in the density of defects and a decrease in the size of structural elements took place. These factors have affected the mechanical properties of the TiNi alloy. The calculation of the contributions to strengthening and comparison with the test results showed that for the coarse-grained state the difference in theoretical and predicted values is not so significant, while for the ultrafine-grained state the difference between the calculated values and the experimental ones is more than 20%.

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