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The influence of hydrogen on the mechanical and functional properties of TiNi and TiNiFe single crystals

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Abstract. The effect of hydrogen on temperature dependence of critical stress $\sigma_{cr}(T)$, the shape memory effect and superelasticity for $[\bar{1}11]$ -oriented single crystals of Ti-50.7Ni (at.%) and $[\bar{1}23]$ -oriented single crystals of Ti-49%Ni-1%Fe (at.%) alloys at tensile deformation has been studied. It was shown that the change of temperatures of the martensitic transformation, symmetry of thermal hysteresis and level of $\sigma_{cr}(M_s)$ and $\sigma_{cr}(B2)$ stresses are determined by the phase state of the material (martensite or austenite) in the process of hydrogenation.

1. Introduction

Nickel titanium (TiNi) alloys are used in technology and medicine due to their unique functional properties, such as shape memory effect (SME) and superelasticity (SE) [1-2]. It is known, that titanium and nickel are hydride-forming materials. Conducted investigations on single- and polycrystals TiNi have shown [2-5], that hydrogen changes start temperature of the direct martensitic transformation (MT) on cooling M_s , decreases the stability of the crystal lattice of the high-temperature B2- phase, and reduces the plasticity. In addition, the observed effects after hydrogenation in TiNi alloys are dependent on the phase, which saturated with hydrogen. The martensitic phase absorbs hydrogen in greater quantities than the high-temperature phase at same conditions of hydrogenation [6]. However, systematic studies for compare the effects of hydrogen on the temperature MT and, respectively, on the mechanical and functional properties of TiNi-based alloys during hydrogenation of martensitic and austenitic phases was not conducted. Therefore, the purpose of the present work is investigation of the effect of hydrogen on temperature dependence of critical stress, $\sigma_{cr}(T)$, in the temperature range $T = 173-473K$, SME and SE in single crystals of Ti-50.7%Ni (at.%) and Ti-49%Ni-1%Fe (at.%) alloys at tensile strain in a single-phase state.

The choice of composition of TiNi alloys is due to the following circumstances. Firstly, in Ti-50.7%Ni single crystals observed one-stage B2-B19' MT with start and finish temperatures for the direct on cooling and the reverse on heating MT: $M_s = 175K$, $M_f = 133K$, $A_s = 192K$, $A_f = 223K$. At room temperature this alloy is in high-temperature B2-phase. This allows us to investigate the effect of hydrogen on the properties of high-temperature phase and MT during hydrogenation of the high-temperature B2-phase. Secondly, Ti-49%Ni-1%Fe single crystals exhibit a two-stage MT through a intermediate R-phase: B2-R-B19' MT [1], with MT temperatures: $M_s = 276K$, $M_f = 260K$, $A_s = 307K$, $A_f = 322K$. At room temperature this alloy is in the martensitic state. This allows us to investigate the effect of hydrogen on the properties of high-temperature phase and MT when saturated with hydrogen of the martensitic phase. At last, thirdly, the choice Ti-50.7%Ni and Ti-49%Ni-1%Fe alloys will allow



to find out the influence of R-phase on B2-B19'- MT after hydrogenation. The $[\bar{1}11]$ - and $[\bar{1}23]$ -oriented single crystals for studying the influence of hydrogen on the SME and SE were selected due to maximum value of the lattice deformation, ε_0 , respectively, $\varepsilon_0=9.8\%$ and $\varepsilon_0=6\%$ [7]. The study on single crystals allows excluding inhomogeneity of hydrogen distribution between grain boundaries and grain body.

2. Materials and discussion of the results

Single crystals of Ti-50.7%Ni and Ti-49%Ni-1%Fe(at.%) alloys were grown by the Bridgeman technique in an inert gas atmosphere. After growing samples of single crystals was homogenized at $T=1173\text{K}$ in a helium atmosphere for 12 hours, followed by water quenching at room temperature. The crystal orientation and phase analysis of the samples were determined on a diffractometer DRON-3 using Fe α -radiation. The samples were cut in the form of double pads with $12 \times 2.5 \times 1 \text{ mm}^3$ working part dimensions. Hydrogenation performed electrochemically in solution of $1\text{M H}_2\text{SO}_4$ at a temperature $T=295\text{K}$, and current density $j=1400 \text{ A/m}^2$ with using an anode made austenitic stainless steel. MT temperatures were determined from inflections on temperature dependences of electric resistivity $\rho(T)$. The mechanical tensile tests were performed on an Instron-5969 machine at a deformation rate of $4 \times 10^{-4} \text{ s}^{-1}$.

Figure 1 shows the temperature dependence of the critical stress $\sigma_{cr}(T)$ for tensile deformation in single crystals measured before and after hydrogenation at room temperature for 2 hours while the current density $j = 1400 \text{ A/m}^2$.

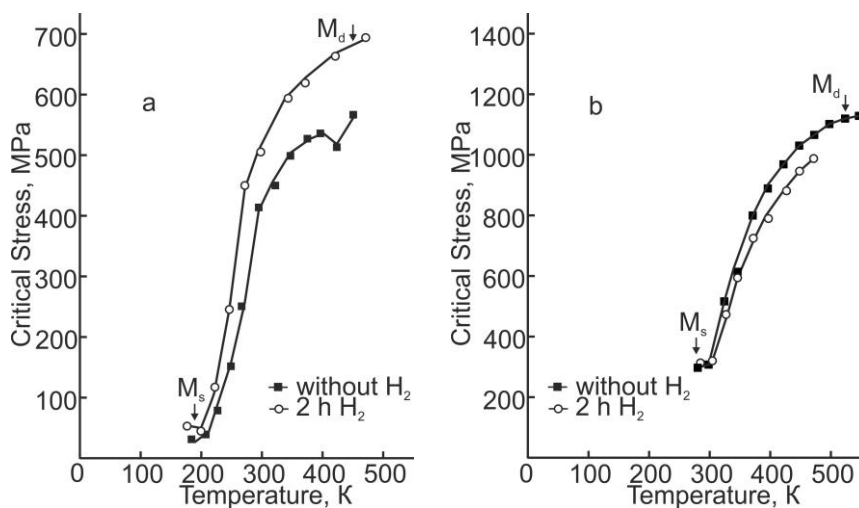


Figure 1. Temperature dependences of critical stress σ_{cr} in $[\bar{1}11]$ -oriented single crystals of Ti-50.7Ni alloy (a) and $[\bar{1}23]$ -oriented single crystals of Ti-49Ni-1Fe alloy (b) at tensile deformation.

It can be seen, that in both cases the $\sigma_{cr}(T)$ dependence has a staging, analogous to those usually observed in the alloys with stress-induced MT [1]. The minimum stresses on the $\sigma_{cr}(T)$ curve are observed at $T=M_s$, which coincides with temperature M_s , determined from the $\rho(T)$ curve. The maximum σ_{cr} stresses corresponds to M_d temperature, at which the stress for start of stress-induced MT is equal to the plastic flow stress of the high-temperature B2- phase. The stage at $M_s < T < M_d$ is characterized by an anomalous temperature dependence $\sigma_{cr}(T)$, which is due to the stress-induced nucleation of B19' martensite crystals [1]. The dependence $\sigma_{cr}(T)$ at this stage is described by the Clapeyron-Clausius equation:

$$\frac{d\sigma_{cr}}{dT} = -\frac{\Delta H}{\varepsilon_0 T_0}, \quad (1)$$

where ΔH is the enthalpy change at B2-B19' MII; ε_0 is the lattice deformation at B2-B19' MT; which depends on the orientation; T_0 is temperature of chemical equilibrium of B2 and B19' phases. At $T > M_d$ on the curve $\sigma_{cr}(T)$ is observed a stage, which is related to the plastic deformation of a high-temperature B2- phase.

When hydrogenation of crystals are at room temperature in a high-temperature phase (Ti-50.7Ni single crystals) for 2 hours and current density $j = 1400 \text{ A/m}^2$ the following relationships detected. Firstly, at the hydrogenation the start temperature M_s is increased as compared to the initial state without hydrogen at 25K. The increase of M_s temperature after hydrogenation of single crystals agrees with the data obtained earlier in the hydrogenation of polycrystalline alloys of similar composition under similar conditions of hydrogenation [8]. However, when hydrogenation of single crystals TiNi alloys this composition at a current density of $j = 700 \text{ A/m}^2$, on the contrary, it was observed a decrease in M_s temperature [4]. Consequently, the temperature M_s is sensitive to hydrogenation modes. Secondly, the hydrogen increases σ_{cr} at a temperature $T=M_s$ from 25 MPa to 40 MPa. Third, hydrogen increases the value of $\alpha = d\sigma_{cr}/dT$: from 4.26 MPa/K for hydrogen-free crystals to 4.6 MPa/K for hydrogenated crystals. At last, fourth, the hydrogenation at a current density $j = 1400 \text{ A/m}^2$ for 2 hours leads to an increase in critical stress of high-temperature B2- phase. The increase stresses during hydrogenation is $\sigma_{cr}^H(400) - \sigma_{cr}(400) = 120 \text{ MPa}$ ($\sigma_{cr}(400)$ - critical stress of high-temperature B2- phase at $T = 400 \text{ K}$ in a state before hydrogenation, $\sigma_{cr}^H(400)$ - after hydrogenation). At the same time the change of the phase composition of Ti-50.7Ni single crystals after hydrogenation at a current density of $j = 1400 \text{ A/m}^2$ for 2 hours by electron microscopy and X-ray is not detected. It follows that hydrogen is in a state of solid solution at hydrogenation of high-temperature B2- phase at a current density $j = 1400 \text{ A/m}^2$ for 2 hours.

Table 1. Mechanical and functional characteristics of $[\bar{1}11]$ -oriented single crystals of Ti-50.7Ni alloy and $[\bar{1}23]$ -oriented single crystals of Ti-49Ni-1Fe alloy.

	Ti-50.7%Ni		Ti-49%Ni-1%Fe	
	Without H ₂	2 h H ₂	Without H ₂	2 h H ₂
Temperature M_s , (K) at $\sigma_{ext} = 0 \text{ MPa}$:	175	200	276	280
MT temperatures at σ_{ext} :	$\sigma_{ext} = 75 \text{ MPa}$		$\sigma_{ext} = 250 \text{ MPa}$	
M_s^σ (K)	214	207	300	310
M_f^σ (K)	178	117	249	257
A_s^σ (K)	235	216	313	311
A_f^σ (K)	272	268	363	365
Interval of direct stress-induced MT (supercooling) $\Delta_1 = M_s - M_f$ (K)	36	90	51	53
Interval of reverse stress-induced MT (superheating) $\Delta_2 = A_f - A_s$ (K)	37	52	50	54
The value of direct thermal hysteresis under stress $\Gamma_1 = A_f - M_s$ (K)	58	61	63	55
The value of reverse thermal hysteresis under stress $\Gamma_2 = A_s - M_f$ (K)	57	99	64	54
$\sigma_{cr}(M_s) / \sigma_{cr}(400)$ (MPa)	25/530	40/650	-	-
$\sigma_{cr}(M_s) / \sigma_{cr}(475)$ (MPa)	-	-	300/1065	315/980
$\alpha = d\sigma_{cr}/dT$ (MPa/K)	4.26	4.6	5.9	5.2

When hydrogenation for 2 hours and the current density $j = 1400 \text{ A/m}^2$ of single crystals (Ti-49Ni-1Fe crystals) which are at room temperature in the martensitic state, is detected, firstly, that temperature M_s and critical stress σ_{cr} at $T = M_s$ increase less, than in crystals Ti-50.7%Ni, during hydrogenation under the same conditions, respectively, 4K and 15 MPa. $\alpha = d\sigma_{cr}/dT$ decrease after hydrogenation from 5.9 MPa/K to 5.2 MPa/K. Secondly, at hydrogenation for 2 hours in Ti-49Ni-1Fe crystals observed the decrease of stress of high-temperature B2- phase: $\sigma_{cr}(475) - \sigma_{cr}^H(475) = 85 \text{ MPa}$, that is the effect of a softening is observed. Ti-50.7Ni single crystals after hydrogenation of high-temperature phases at room temperature at current density of $j = 1400 \text{ A/m}^2$ the softening effect has

been observed at higher hydrogenation times [5]. It was associated with the formation of TiNi_3 and TiH particles during hydrogenation, as shown by X-ray diffraction phase analysis and transmission electron microscopy [5,9]. Therefore, it is believed that lowering the strength properties of high-temperature phase at hydrogenation of Ti-49Ni-1Fe single crystals in the martensitic state at room temperature occurs due to the change in the phase composition of these crystals at hydrogenation.

Figure 2 presents results of investigation of the SME effect during cooling/heating under tensile stresses in test temperatures interval 77–400K. Such experiments allow determining the influence of external stresses σ_{ext} not only on the MT temperatures, but also on the thermal hysteresis ΔT and the value of transformation strain ε_{tr} . The value of external tensile stress for both alloys was equal to, respectively, the tensile stress at $T = M_s$, obtained from studying the temperature dependence of $\sigma_{\text{cr}}(T)$.

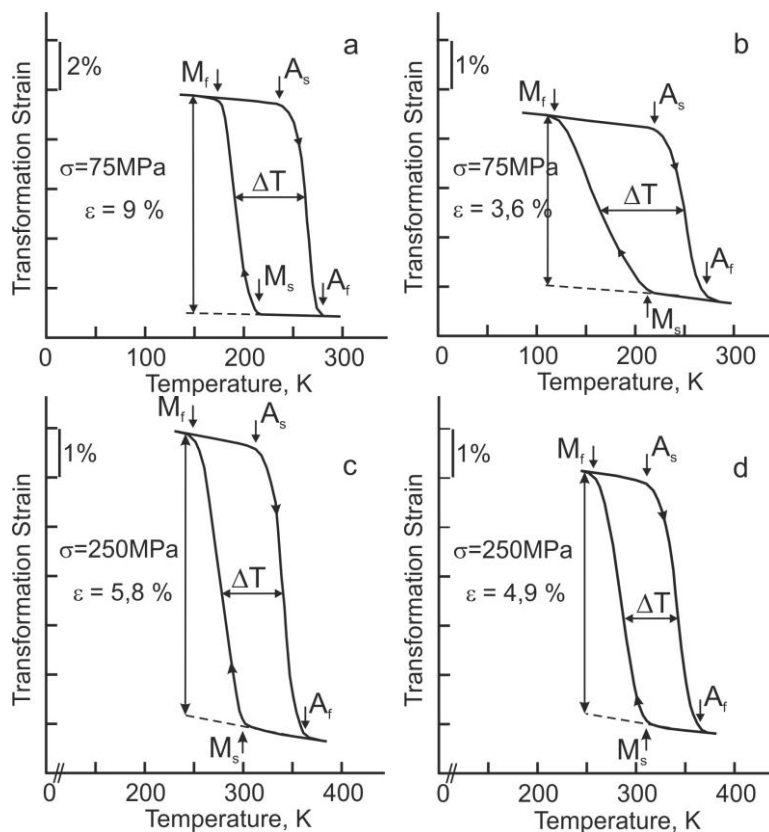


Figure 2. Value of SME at constant tensile stress in $[\bar{1}11]$ -oriented single crystals Ti-50.7Ni alloy (a,b) and $[\bar{1}23]$ -oriented single crystals Ti-49Ni-1Fe alloy (c,d): (a,c) in the absence of hydrogen; (b,d) upon hydrogenation at $T = 295\text{K}$ and current density $j = 1400\text{ A/m}^2$ for 2 hours.

As can be seen for $[\bar{1}11]$ -oriented single crystals of Ti-50.7Ni alloy, which are in the B2- phase at room temperature, both hydrogen-free and hydrogenated crystals at $\sigma_{\text{ext}} = 75\text{ MPa}$ is realized single-stage B2–B19' MT, that is fully reversible upon heating, and the SME is observed. The value of SME effect ε_{SME} in hydrogen-free $[\bar{1}11]$ -oriented single crystals is 9% and close to theoretically calculated value of lattice deformation $\varepsilon_0 = 9,8\%$ in $[\bar{1}11]$ -orientation for B2–B19' MT at tension [7]. In the hydrogenated material at $\sigma_{\text{ext}} = 75\text{ MPa}$ the value of ε_{SME} is 2.5 times lower than in the crystals without hydrogen. That is to cause fracture of the self-accommodating B19' -martensite structure in hydrogenated crystals these stresses are insufficient as compared with crystals without hydrogen. Therefore, hydrogen increases the resistance to motion of the intervariant and twin boundaries in martensite as compared with the hydrogen-free state. This agrees with the increasing the value of $\sigma_{\text{cr}}(M_s)$. In order to reach the theoretical values of the lattice deformation in the hydrogenated crystals, it is necessary to increase external stresses of B2–B19' MT.

In $[\bar{1}23]$ -oriented single crystals of Ti-49Ni-1Fe alloy, which are in the martensitic phase at room temperature, both in hydrogen-free and hydrogenated crystals at $\sigma_{\text{ext}} = 250\text{ MPa}$ is realized single-stage B2–B19' MT, that is fully reversible upon heating, and the SME is observed. B2-R MT appears

at much lower stresses, and in this work is not considered. In hydrogen-free $[\bar{1}23]$ -oriented single crystals of Ti-49Ni-1Fe alloy at $\sigma_{\text{ext}} = 250$ MPa the value transformation strain $\varepsilon_{\text{SME}} = 5,8\%$ and is close to the theoretically calculated value of the lattice deformation $\varepsilon_0 = 6\%$ in $[\bar{1}23]$ -orientation for B2–B19' MT at tension [7], which is a qualitative confirmation of stress-induced B2–B19' MT in Ti-49Ni-1Fe crystals at $\sigma_{\text{ext}} = 250$ MPa. After hydrogenation the value of deformation strain decreases at $\sigma_{\text{ext}} = 250$ MPa and becomes equal to 4.9%.

The table 1 shows the mechanical and functional characteristics of the B2–B19' MT for Ti-50.7Ni and Ti-49Ni-1Fe crystals, obtained in experimental studies of SME under stress. It is visible, that in hydrogen-free Ti-50.7Ni crystals the values of supercooling $\Delta_1 = M_f - M_s = 36\text{K}$ and superheating $\Delta_2 = A_s - A_f = 37\text{K}$ and the value of thermal hysteresis $\Gamma_1 = A_f - M_s = 58\text{K}$ and $\Gamma_2 = A_s - M_f = 57\text{K}$ are equal to each other. As a result of thermal hysteresis loop is symmetric: $\Delta_1/\Delta_2 = 0.97$, $\Gamma_1/\Gamma_2 = 1.02$. Hydrogenation increases Δ_1 , Δ_2 , Γ_1 and Γ_2 as compared to the state without hydrogen (Table 1, Figure 2.b) due to the influence of the M_f temperature which is shifted to lower temperatures in 61K. As a result, for hydrogenated of Ti-50.7Ni crystals the thermal hysteresis loop has an asymmetrical form: $\Gamma_1 < \Gamma_2$ ($\Gamma_1 = 61$ K, $\Gamma_2 = 99$ K).

In $[\bar{1}23]$ -oriented single crystals of Ti-49Ni-1Fe alloy thermal hysteresis both in the initial state and after hydrogenation is symmetric: in hydrogen-free crystals – $\Delta_1/\Delta_2 = 1.02$, $\Gamma_1/\Gamma_2 = 0.98$, after hydrogenation – 0.98 and 1.02, respectively. It should be noted, that in hydrogenated Ti-49Ni-1Fe crystals observed narrowing trend of thermal hysteresis by increasing the M_s and M_f temperatures under stress, respectively, on 10K and 8K, compared with crystals without hydrogen.

Analysis of the data shows, that the characteristics of the B2-B19' MT depend on the condition of the crystal during hydrogenation. Thus, if the crystal during hydrogenation at room temperature is in the high-temperature B2- phase, the hydrogenation accompanied by a change of the form of thermal hysteresis loops from symmetric in hydrogen-free state to asymmetric after hydrogenation and a value of Γ_2 increased. If the crystal during hydrogenation at room temperature is in the martensitic phase, form of thermal hysteresis loop after hydrogenation remains symmetrical, as in the state without hydrogen and thermal hysteresis on the contrary decreases. And this is determined by the presence of R- phase in Ti-49Ni-1Fe crystals and its absence in Ti-50.7Ni crystals. R- phase apparently slows down the effect of hydrogen on the characteristics of the MT as a result of the weak impact of hydrogen on the R- phase.

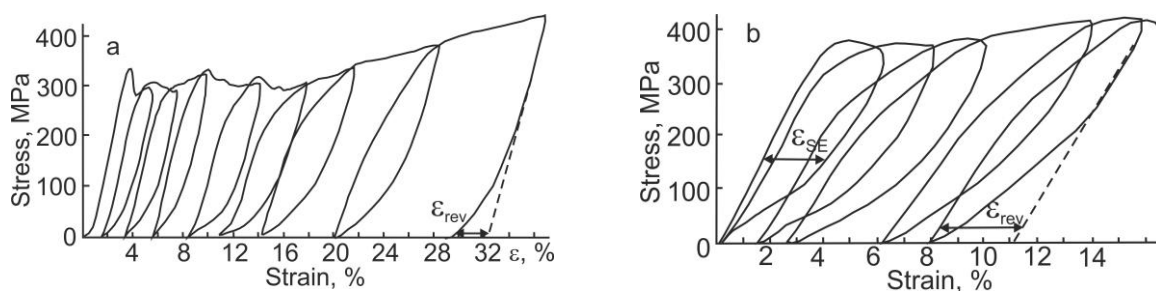


Figure 3. Stress-strain curve at tension for $[\bar{1}11]$ -oriented single crystals of Ti-50.7Ni (at. %) alloy in hydrogen-free state (a) and after hydrogenation (b); test temperature 275K, $A_f = 223\text{K}$.

In $[\bar{1}11]$ -oriented hydrogen-free crystals of Ti-50.7Ni alloy the SE is not observed (Figure 3.a). At a preset strain of $\varepsilon_{\text{exp}} = 2.5\%$ in the first cycle at test temperature $T = 275\text{K}$, a perfect loop is not formed, and reversible deformation $\varepsilon_{\text{rev}} = 1\%$. At $\varepsilon_{\text{exp}} = 35\%$ the ε_{rev} increases to 2.5%, and at a further increase to $\varepsilon_{\text{exp}} > 35\%$ the crystal is not destroyed. After hydrogenation for 2 h., when the hydrogen in the crystal is a solid solution the SE equal to 2.5% is observed at $T = 275\text{K}$ (Figure 3.b). With increasing ε_{exp} to 12.5% ε_{rev} becomes 3%. After $\varepsilon_{\text{exp}} > 12.5\%$ hydrogenated crystals are destroyed. In $[\bar{1}23]$ -oriented hydrogen-free crystals of Ti-49Ni-1Fe alloy the SE was not detected. At a preset strain of $\varepsilon_{\text{exp}} = 3\%$ in the first cycle at test temperature $T = 345\text{K}$ the reversible deformation $\varepsilon_{\text{rev}} = 1\%$.

At $\varepsilon_{\text{exp}} = 10\%$ the ε_{rev} becomes equal 2.5%, and a further increase in $\varepsilon_{\text{exp}} > 10\%$ the crystal is destroyed. After hydrogenation at $\varepsilon_{\text{exp}} = 2.5\%$ at $T = 345\text{K}$ reversible strain $\varepsilon_{\text{rev}} = 1.6\%$. At $\varepsilon_{\text{exp}} > 2.5\%$ crystals are destroyed. This sharp decline of plasticity in TiNi crystals associated with the advent of titanium hydrides [5].

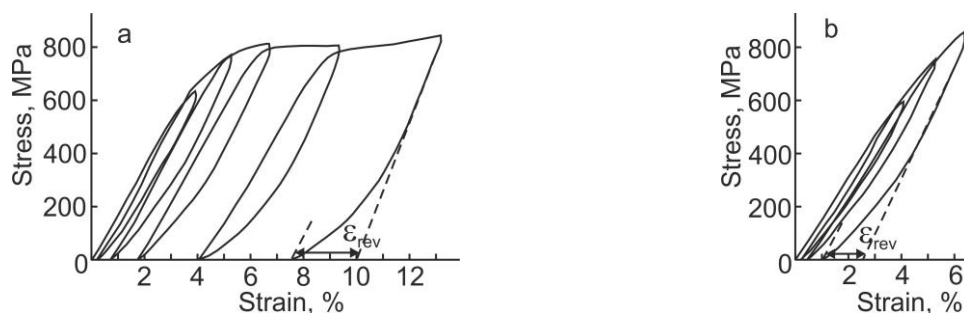


Figure 4. Stress-strain curve at tension for $[\bar{1}23]$ -oriented single crystals of Ti-49Ni-1Fe alloy: (a) in hydrogen-free state, (b) after hydrogenation; test temperature 345K, $A_f = 322\text{K}$.

3. Conclusion

It was established experimentally, that the mechanical and functional properties of single crystals of TiNi alloys depend on the phase state (martensite or high-temperature phase), at which electrochemical hydrogenation in 1M solution of H_2SO_4 at $T = 295\text{K}$ and current density $j = 1400\text{ A/m}^2$ for 2 hours occurs.

The hydrogenation of $[\bar{1}11]$ -oriented single crystals of Ti-50.7%Ni (at. %) alloy, which are in a high-temperature B2- phase at room temperature, increases the start temperature of the MT upon cooling M_s , increases a stress σ_{cr} in the point M_s and in the high-temperature B2- phase, increases of the thermal hysteresis, leads to asymmetrical loop form of thermal hysteresis, to decrease of the plasticity and to appearance of SE equal 2.5% compared with hydrogen-free crystals.

The hydrogenation of $[\bar{1}23]$ -oriented single crystals of Ti-49%Ni-1%Fe (at. %) alloy, which are in martensitic phase at room temperature, leads to an increase of temperature M_s and stress $\sigma_{\text{cr}}(M_s)$, to decrease of the thermal hysteresis while maintaining its symmetry, to decrease a stress of the high-temperature B2- phase, and the plasticity compared with hydrogen-free crystals.

This difference in behavior TiNi crystals due, apparently, to the difference in the hydrogenation of high-temperature phase and martensite.

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