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Effect of martensite ageing on the orientation dependence of the $B2$-phase yield stress and the shape memory effect in Ti−40Ni−10Cu alloy single crystals

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For the [001]- and [$\bar{1}$23]-oriented single crystals of the Ti−40Ni−10Cu alloy, it was shown for the first time that martensite ageing at 250 MPa leads to a strong orientation dependence of the $B2$-phase yield stress under tension, which is weakly manifested in the initial crystals. The maximum increase in the $B2$-phase yield stress by 350 MPa compared with the initial state was found in the [001]-oriented crystals. At external tensile stresses of 100 MPa, the shape memory effect in [001]-oriented crystals was $4.0 \pm 0.2\%$ in the initial state and increased to $5.0 \pm 0.2\%$ after martensite ageing, while in [$\bar{1}$23] orientation, on the contrary, it decreased from $8.7 \pm 0.2\%$ to $5.4 \pm 0.2\%$.

Keywords: Single crystals, Martensite ageing, B2-phase, Shape memory effect, Tension.

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Ti−Ni alloys are widely known for their unique properties: shape memory effect (SME) and superelasticity [1,2]. A high stability of superelasticity and SME in cyclic tests, which is needed in medical and engineering applications, is achieved in these alloys due to a high level of stresses of the high-temperature $B2$ phase at yield stress ($\sigma_{0.1}(B2)$) [1]. The yield stress of the $B2$ phase in Ti−Ni alloys may be enhanced in various ways: by precipitation hardening, via prestraining in the high-temperature phase (ausforming) or martensite (marforming) with subsequent low-temperature annealing, by doping with Zr, Hf, Pd, Au, Co, and Cu atoms, etc. [1–5]. In the present study, were use single crystals of the Ti−40Ni−10Cu (at.%) alloy with two orientations ([001] and [$\bar{1}$23]) to examine the influence of martensite ageing under a tensile load of 250 MPa on stresses $\sigma_{0.1}(B2)$ and the SME magnitude under tension. The Ti−40Ni−10Cu alloy is characterized by a two-stage martensitic transformation (MT): $B2-B19-B19'$ [1]. Only the $B2-B19$ MT with lattice strain $\varepsilon_0 = 3.49\%$ is induced under tension in orientation [001] under load, while orientation [$\bar{1}$23] undergoes the $B2-B19-B19'$ MT with $\varepsilon_0 = 7.22\%$ [6].

Single crystals of the Ti−40Ni−10Cu were grown by the Bridgman method in helium. Their orientation was determined using a DRON-3M diffractometer and FeK_α radiation. Dumb-bell samples $2 \times 1.5 \times 15$ mm in size were cut out using an electrospark discharge machine. Samples were homogenized in helium at 1073 K for 14 h and quenched in water. After quenching, the crystals had the following MT temperatures: $M_s^1 = 312$ K, $M_f^1 = 289$ K, $A_s^1 = 300$ K, and $A_f^1 = 322$ K for the first $B2-B19$ transition; $M_s^2 = 263$ K, $M_f^2 = 175$ K, $A_s^2 = 219$ K, and $A_f^2 = 270$ K for the second $B19-B19'$ transition (M_s, M_f are the temperatures of initiation and end of the direct MT under cooling, respectively, and A_s, A_f are the temperatures of initiation and end of the reverse MT under heating, respectively). The temperature dependence of stresses $\sigma_{0.1}(T)$ was examined at an Instron 5969 testing system with a strain rate of $4 \cdot 10^{-4}\,s^{-1}$. The shape memory effect and martensite ageing under load were studied using a dilatometer under cooling and heating within the 77-400 K temperature interval at constant tensile stresses in a cycle and a heating/cooling rate of 10 K/min. Electron microscopic studies were carried out using a Jeol 2010 microscope at an accelerating voltage of 200 kV.

Data on martensite ageing of single crystals with orientations [001] and [$\bar{1}$23] under a tensile stress of 250 MPa are presented in Figs. 1, *a* and *b*. The sample under load was cooled to 77 K to complete the transformation. Heating to a temperature corresponding to the onset of reverse transitions $B19-B2$ and $B19'-B19-B2$ in [001] and [$\bar{1}$23] crystals, respectively, was performed next (the holding temperature is indicated by filled circles on the curves). The sample under load was held at this temperature for 2 h. The load was then removed, and the irreversible strain was measured at 296 K. It can be seen from Figs. 1, *a* and *b* that transformation strain ε_{tr} was 6.5 ± 0.2 and $8.5 \pm 0.2\%$ for crystals with orientations [001] and [$\bar{1}$23], respectively, subjected to cooling under load. Experimental ε_{tr} values turned out to be higher than theoretical values ε_0 for the corresponding orientation; specifically, $\varepsilon_{tr} = 6.5 \pm 0.2\%$ in orientation [001] was almost two times higher than $\varepsilon_0 = 3.49\%$ for the $B2-B19$ MT, while ε_{tr} in orientation [$\bar{1}$23] for the $B2-B19-B19'$ MT was just $1.28 \pm 0.2\%$ greater than $\varepsilon_0 = 7.22\%$ [6]. Experimental ε_{tr} values exceed the theoretical ε_0 value due to $\langle 011\rangle\{110\}_{B19}$ twinning in $B19$ martensite, which is reversible under heating,

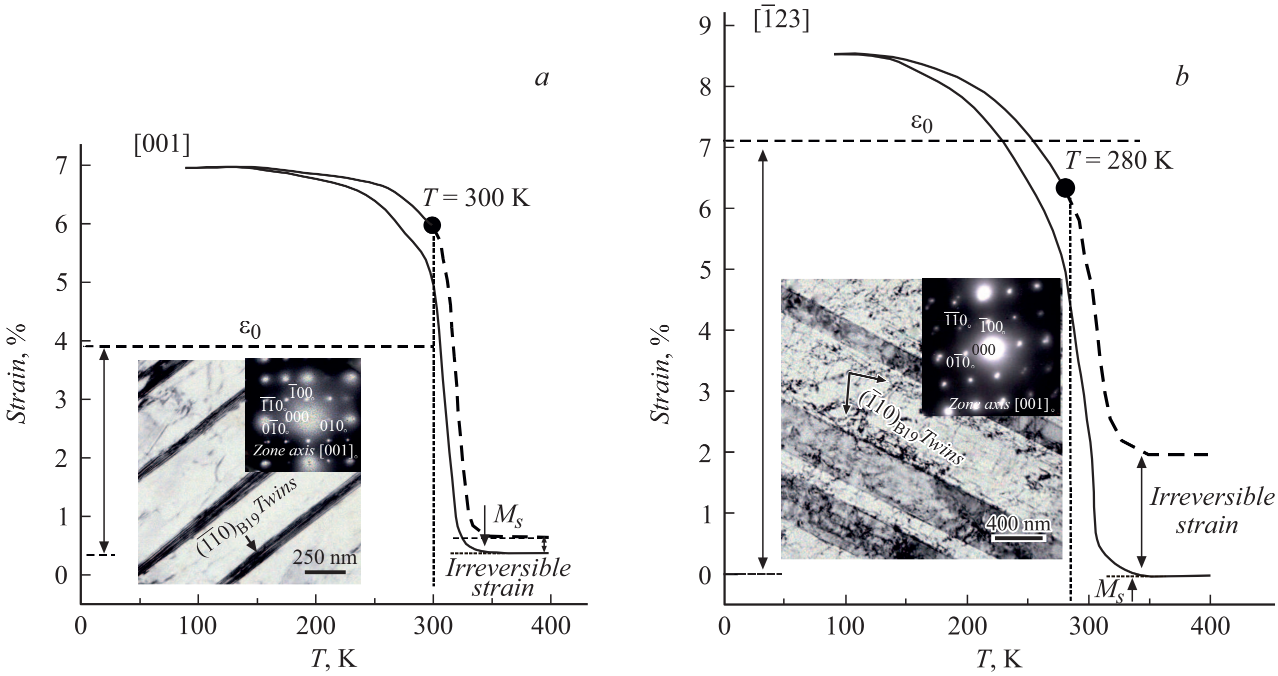

Figure 1. Martensite ageing of single crystals of the Ti$-$40Ni$-$10Cu alloy under external tensile stresses of 250 MPa. *a* — Orientation [001], *b* — orientation [$\bar{1}$23]. The horizontal dashed line denotes the theoretical value of transformation strain ε_0 for the $B2-B19$ and $B2-B19-B19'$ MTs in orientations [001] and [$\bar{1}$23], respectively. The microstructure after martensite ageing for the corresponding orientation of single crystals of the Ti$-$40Ni$-$10Cu alloy is shown in the insets.

under load [7]. The irreversible strain measured 2 h after the removal of load was 0.2 and 2% for crystals with orientations [001] and [$\bar{1}$23], respectively. Onset temperature $M_s = 313$ K of the first $B2-B19$ transition under cooling after martensite ageing remained the same as the one in the initial state. The results of electron microscopic studies of the microstructure after martensite ageing in orientation [001] revealed $B19$ martensite with $\{110\}_{B19}$ twins (inset in Fig. 1, *a*), and $B19$ martensite with $\{110\}_{B19}$ twins and a high dislocation density were observed in orientation [$\bar{1}$23] (inset in Fig. 1, *b*). This difference in defect structures and the irreversible strain magnitude is attributable to the ease of development of local plastic strain by slip in the course of MT under load and high stresses in crystals with orientation [$\bar{1}$23] and the relative suppression of slip in crystals with orientation [001]. Crystals with orientation [$\bar{1}$23] are characterized by Schmid factor $m_{sl} = 0.46$ for slip systems $a\langle 100\rangle\{001\}$ in $B2$ alloys, while crystals with orientation [001] feature $m_{sl} = 0$ and suppressed slip in the $B2$ phase [6].

Temperature dependences $\sigma_{0.1}(T)$ in crystals of the Ti$-$40Ni$-$10Cu alloy with two different orientations after quenching and martensite ageing at 250 MPa have the form typical of alloys that undergo an MT under load [1] (Fig. 2). The $\sigma_{0.1}(T)$ dependence has its minimum at temperature M_s, which is equal to temperature M_s determined based on the temperature dependence of resistance $\rho(T)$. The maximum of the $\sigma_{0.1}(T)$ dependence corresponds to temperature M_d at which stresses $\sigma_{0.1}$ for the MT onset under load ($\sigma_{0.1}$(SIM)) are equal to stresses $\sigma_{0.1}$ for the onset of plastic flow of the $B2$ phase ($\sigma_{0.1}(B2)$). A near-linear stage, which is related to the evolution of MT under load, is observed in temperature interval $M_s < T < M_d$. This stage is characterized by the Clausius$-$Clapeyron relation [1]:

$$\frac{d\sigma_{0.1}(\mathrm{SIM})}{dT} = -\frac{\Delta S}{\varepsilon_{tr}} = -\frac{\Delta H}{\varepsilon_{tr} T_0}. \quad (1)$$

Here, ΔS, ΔH are the variations of entropy and enthalpy in the process of MT, respectively; T_0 is the temperature of chemical phase equilibrium; and ε_{tr} is the transformation strain. It follows from Fig. 2 that, first, martensite ageing under 250 MPa at a low temperature of 280$-$300 K has no effect on $\alpha = d\sigma_{0.1}(\mathrm{SIM})/dT$ in crystals of the same orientation. Second, the value of α depends on orientation, and its orientation dependence is retained after martensite ageing under 250 MPa. Specifically, $\alpha = 6.18$ MPa/K for orientation [001], and $\alpha = 4.5$ MPa/K for [$\bar{1}$23]. The orientation dependence of α is proportional to $1/\varepsilon_{tr}$. Ratio $\alpha([001])/\alpha([\bar{1}23]) = 1.4$ turns out to be close to ratio $\varepsilon_{tr}([\bar{1}23])/\varepsilon_{tr}([001]) = 1.3$. At $T > M_d$, dependence $\sigma_{0.1}(T)$ is governed by the temperature dependence of $\sigma_{0.1}(B2)$. It can be seen that the initial crystals have similar $\sigma_{0.1}(B2)$ levels in both orientations. Following martensite ageing under 250 MPa, the $\sigma_{0.1}(B2)$ values increased by 50$-$65 MPa in orientation [$\bar{1}$23] and by 350 MPa in orientation [001]. A strong orientation dependence of $\sigma_{0.1}(B2)$ emerges as a result. Profound hardening of the $B2$ phase

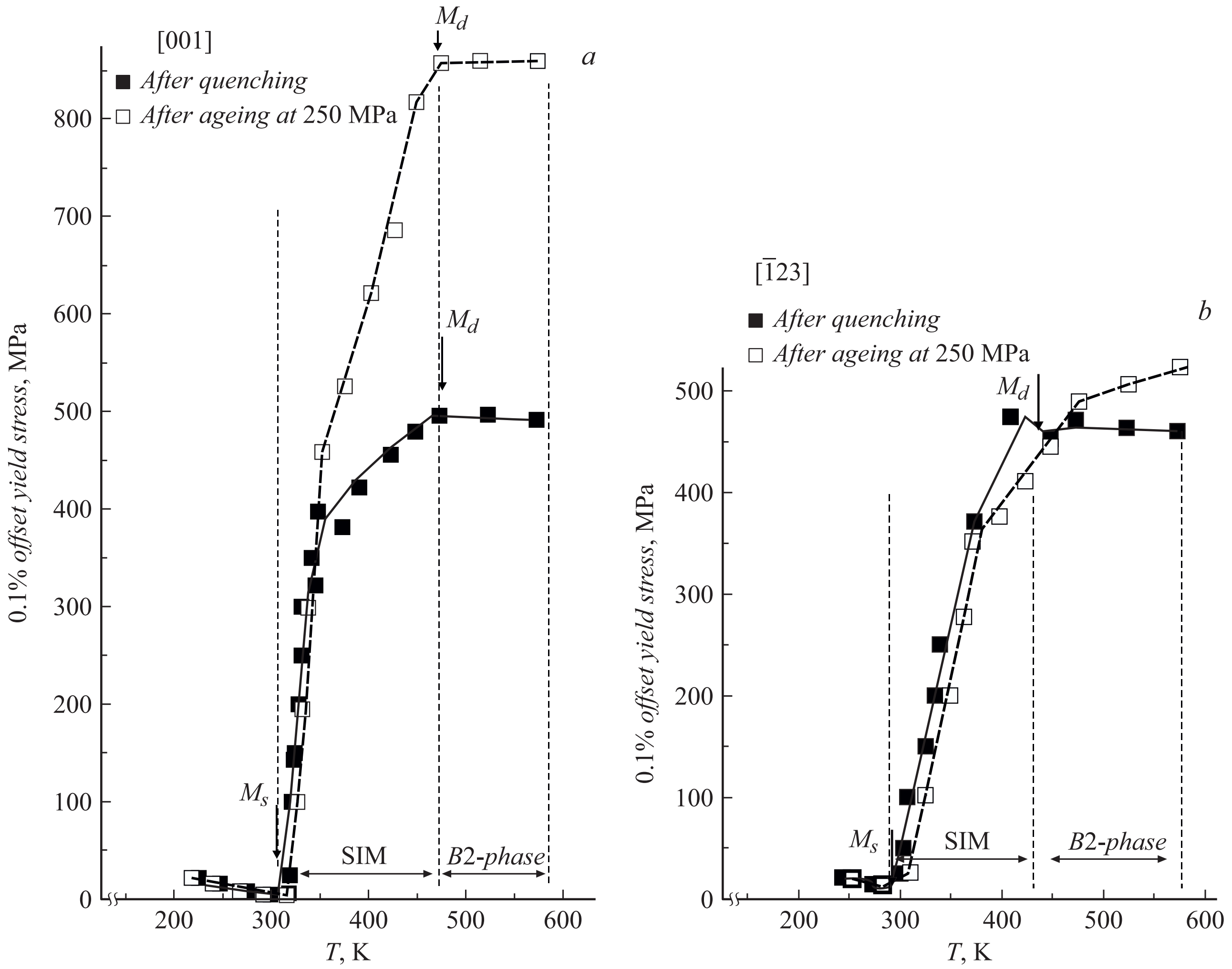

Figure 2. Temperature dependence of stresses $\sigma_{0.1}$ at yield stress of single crystals of the Ti−40Ni−10Cu alloy under tension. *a* — Orientation [001], *b* — orientation [$\bar{1}$23]. Indicated are temperature intervals within which stresses $\sigma_{0.1}$ for the onset of martensite formation under load (SIM) and the onset of plastic strain of the high-temperature $B2$ phase are determined.

in orientation [001] may contribute to the enhancement of functional properties of Ti−40Ni−10Cu alloys.

Indeed, the SME magnitude in orientation [001] after martensite ageing under $\sigma_{ex} = 5-100$ MPa is 1% greater than the one in the initial state after quenching under the same σ_{ex} (Fig. 3, *a*). In the [$\bar{1}$23] orientation, where the yield stress of the $B2$ phase after martensite ageing increases only slightly relative to its value for quenched crystals, the SME magnitude under $\sigma_{ex} = 100$ MPa after martensite ageing becomes $3.3 \pm 0.2\%$ lower than the one in the initial crystals (Fig. 3, *b*). Notably, the SME magnitude of $5.4 \pm 0.2\%$ turns out to be lower than theoretical value $\varepsilon_0 = 7.22\%$ for the $B2-B19-B19'$ MT in orientation [$\bar{1}$23] under tension [6]. It is fair to assume that a high dislocation density after martensite ageing hampers the $B19-B19'$ MT. This is corroborated qualitatively, first, by the SME magnitude of $5.4 \pm 0.2\%$ under $\sigma_{ex} = 100$ MPa, which is close to the theoretical $\varepsilon_0 = 4.9\%$ value for the $B2-B19$ MT under tension in orientation [$\bar{1}$23] [6], and, second, by the SME enhancement (relative to the initial crystals where the $B2-B19$ MT develops without dislocations) in orientation [001] under $\sigma_{ex} = 100$ MPa after martensite ageing under load.

Thus, it has been demonstrated for the first time for single crystals of the Ti−40Ni−10Cu alloy oriented along the [001] and [$\bar{1}$23] directions that martensite ageing under a load of 250 MPa raises yield stress $\sigma_{0.1}(B2)$ of the $B2$ phase and induces a strong orientation dependence of $\sigma_{0.1}(B2)$ under tension (in contrast to quenched crystals, where this dependence is weak). The maximum enhancement of $\sigma_{0.1}(B2)$ after martensite ageing under 250 MPa was 350 MPa (relative to the yield stress for the initial crystals) in orientation [001]. In the initial state after quenching under $\sigma_{ex} = 100$ MPa, the SME magnitude was 4.0 ± 0.2 and $8.7 \pm 0.2\%$ in crystals with orientations [001] and [$\bar{1}$23], respectively. Following martensite ageing under $\sigma_{ex} = 100$ MPa, the SME

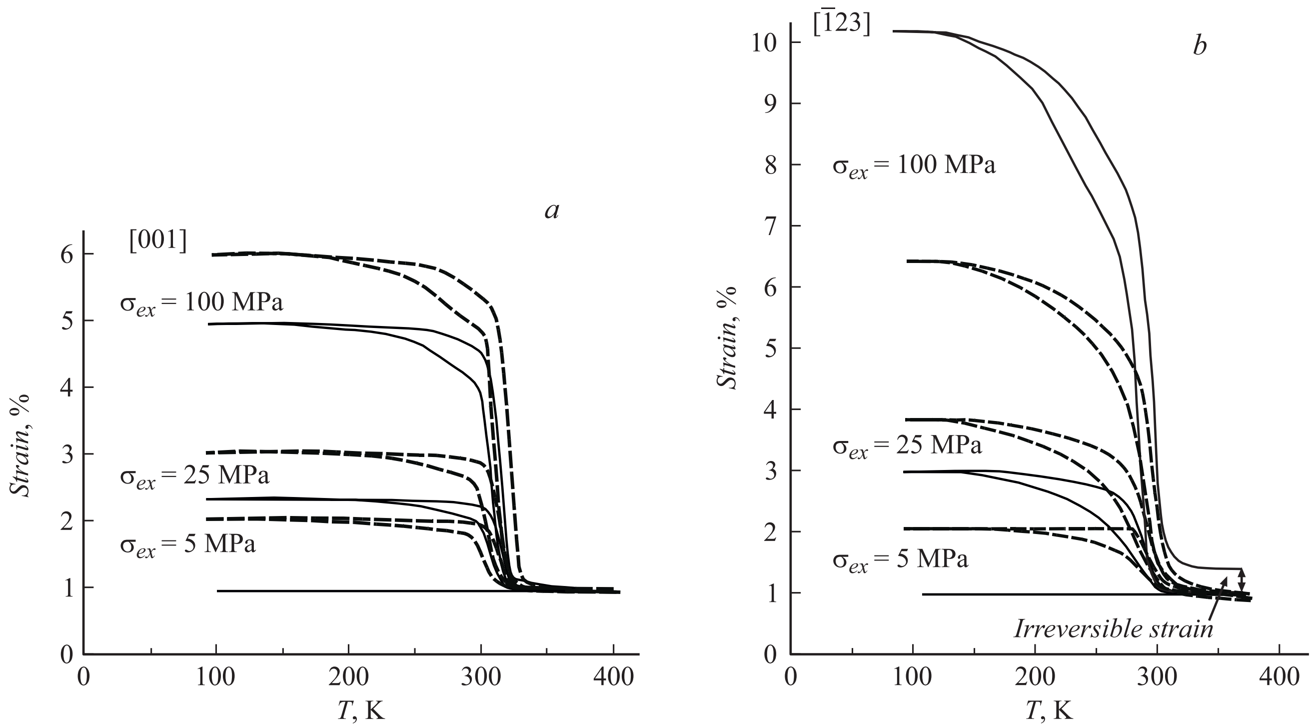

Figure 3. Strain–temperature curves for single crystals of the Ti–40Ni–10Cu alloy under different levels of tensile stresses. *a* — Orientation [001], *b* — orientation [$\bar{1}$23]. Solid and dashed curves correspond to the initial state after quenching and martensite ageing under 250 MPa, respectively.

magnitude became equal to 5.0 ± 0.2 and $5.4 \pm 0.2\%$ in crystals with orientations [001] and [$\bar{1}$23], respectively.

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Conflict of interest

The authors declare that they have no conflict of interest.

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