Technical Physics Letters, 2025, Vol. 51, No. 1

06

Effect of orientation on superelasticity of Fe$-$33Mn$-$11Al$-$7Ni$-$6Cr single crystals with negative temperature dependence of stresses for the onset of transformation

© *Yu.I. Chumlyakov, I.V. Kireeva, Z.V. Pobedennaya, L.P. Yakovleva, I.V. Kuksgauzen, D.A. Kuksgauzen*

Tomsk State University, Tomsk, Russia
E-mail: kireeva@spti.tsu.ru

Received June 13, 2024
Revised July 30, 2024
Accepted July 30, 2024

For the first time, a negative temperature dependence of the stresses of the onset martensitic transformation σ_{Ms} was discovered in the temperature range of 203$-$(275$-$300) K and 325$-$(425$-$475) K in the quenched Fe$-$33Mn$-$11Al$-$7Ni$-$6Cr (at.%) alloy single crystals oriented along $[\bar{1}11]$, $[\bar{1}23]$ and [011] directions, under compression. In the temperature range of (425$-$475)$-$573 K, a positive dependence $\sigma_{Ms}(T)$ was observed. Superelasticity was found in the [011] and $[\bar{1}23]$ orientations in the temperature range of 203$-$573 K, while it was absent in the $[\bar{1}11]$ orientation.

Keywords: Single crystals Fe$-$33Mn$-$11Al$-$7Ni$-$6Cr, thermoelastic martensitic transformation, superelasticity, nano-sized particles.

DOI: 10.61011/TPL.2025.01.60126.20020

Unique functional properties (shape memory effect and superelasticity (SE)) are associated with thermoelastic stress-induced martensitic transformation [1,2]. Ti$-$Ni, Fe$-$Ni$-$Co$-$Al$-X$ ($X = \mathrm{Ta, Nb, Ti}$), and other alloys [1$-$10] are characterized by a positive temperature dependence $\sigma_{Ms}(T)$ of stresses of the MT onset, which follows the Clausius$-$Clapeyron relation

$$\frac{d\sigma_{Ms}(T)}{dT} = -\frac{\Delta H}{\varepsilon_0 T_0} = -\frac{\Delta S}{\varepsilon_0} = \alpha. \qquad (1)$$

Here, ΔH and ΔS are the variations of enthalpy and entropy, respectively, per unit volume in the course of MT; T_0 is the phase equilibrium temperature, and ε_0 is the transformation strain [1,2]. It has been found recently that α decreases to 0.5 MPa/K in Fe$-$Mn$-$Al$-$Ni$-X$ ($X = \mathrm{C, Ti, Mo, Cr}$) alloys, and when chromium concentration C_{Cr} exceeds 5 at.%, α assumes a zero (or even negative) value [3$-$11]. This uncommon temperature dependence of $\sigma_{Ms}(T)$ with stresses σ_{Ms} of the MT onset decreasing with an increase in test temperature is associated with magnetic transformations in the high-temperature phase and martensite in these alloys with $C_{\mathrm{Cr}} \geqslant 5$ at.% [3,4,11].

The aim of the present study was to investigate the influence of crystal orientation on the temperature range within which the SE effect is manifested, the maximum SE magnitude, and temperature dependence $\sigma_{Ms}(T)$ under compression for single crystals of the Fe$-$33Mn$-$11Al$-$7Ni$-$6Cr (at.%) alloy. Orientations $[\bar{1}11]$, $[\bar{1}23]$, and [011] were chosen for analysis. They have different ε_0 values for single crystals of the Fe$-$Mn$-$Al$-$Ni$-$Cr alloy with chromium concentration $C_{\mathrm{Cr}} = 5$$-$7 at.% under compression: $\varepsilon_0([\bar{1}11]) = 2\%$, $\varepsilon_0([011]) = 6\%$, $\varepsilon_0([\bar{1}23]) = 8.5\%$ [3,4].

Single crystals were grown using the Bridgman method from blanks prepared in a resistance furnace. The ingots were remelted five times in an argon environment to obtain a uniform distribution of elements within them. The chemical composition of the obtained crystals was determined using a TESCAN VEGA3 scanning microscope fitted with an AztecLive Lite Xplore 30 energy-dispersive spectroscopy system that provides an elemental composition determination accuracy of 0.03$-$0.05 at.%. It was found that the crystals contained the following elements: Fe — 43 at.%, Mn — 32.7 at.%, Al — 11.2 at.%, Ni — 7.1 at.%, and Cr — 6 at.%. Their orientation was determined with the use of a DRON-3 diffractometer. Samples for compression $6 \times 3 \times 3$ mm in size were cut using an Arta-3 electrospark discharge machine. They were homogenized at 1493 K for 4 h (and further at 1523 K for 2 h) in a helium environment with subsequent quenching in water. The stresses of the BCC$-$FCC MT onset, the temperature range within which the SE effect is manifested, and the maximum SE magnitude under compression were examined with an Instron 5969 testing system at a strain rate of $4 \cdot 10^{-4}\,\mathrm{s}^{-1}$.

Quenched single crystals of the Fe–33Mn–11Al–7Ni–6Cr alloy have a two-phase structure with a BCC matrix and β-phase particles 10$-$15 nm in diameter with an ordered $B2$-type structure [3,4,11].

The results of study of the temperature range within which the SE effect is manifested in single crystals of the Fe$-$33Mn$-$11Al$-$7Ni$-$6Cr alloy under compression at a applied strain of 1$-$1.5% in the loading–unloading cycle are presented in Fig. 1. It is evident that the SE effect is found in single crystals with compression axis [011] and $[\bar{1}23]$ within the temperature range of 203$-$573 K and is lacking in single crystals with compression axis

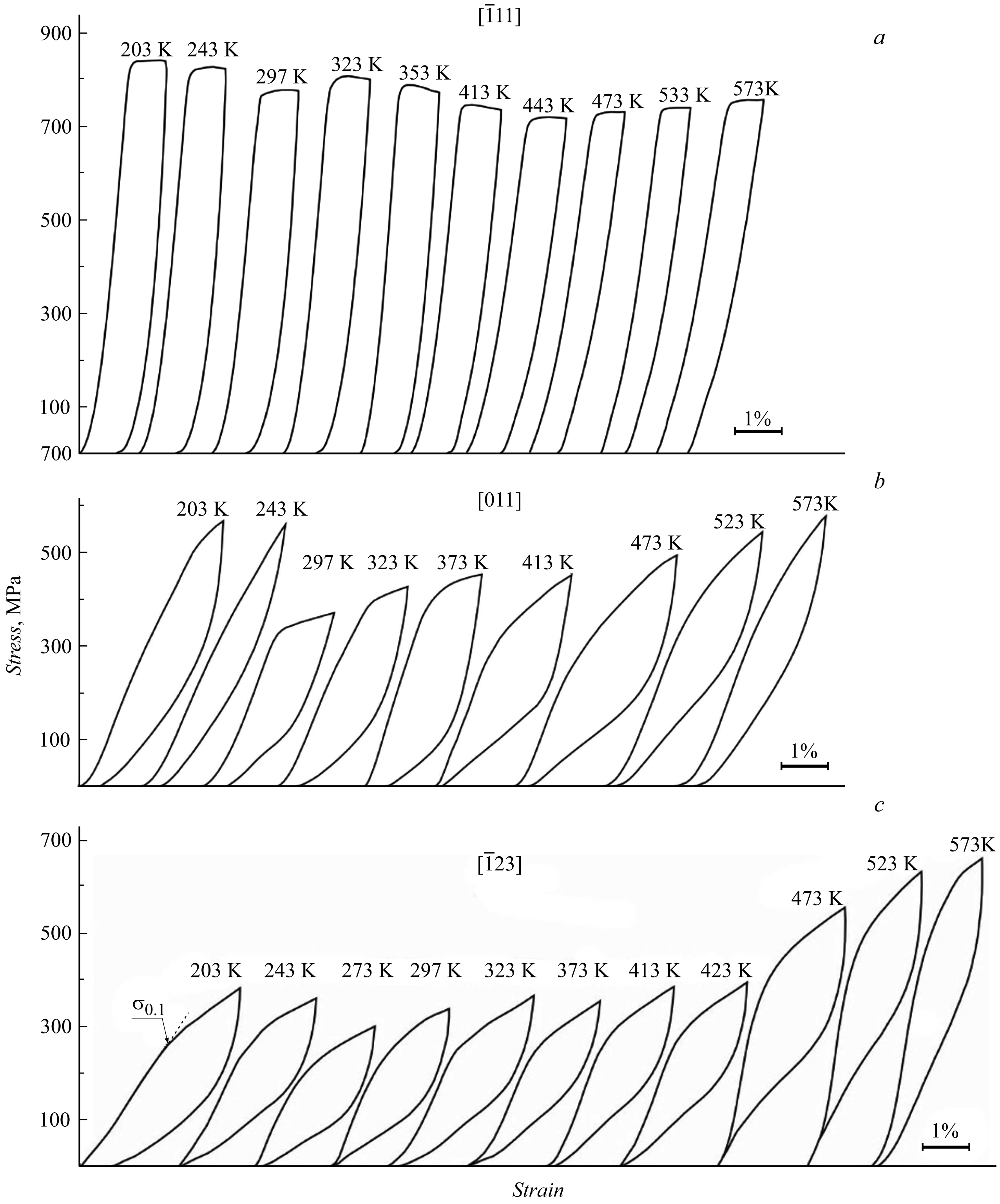

Figure 1. Temperature interval within which the superelasticity effect is manifested in single crystals of the Fe–33Mn–11Al–7Ni–6Cr alloy under compression. *a* — Orientation [$\bar{1}11$]; *b* — [011]; and *c* — [$\bar{1}23$].

[$\bar{1}11$]. Single crystals with compression axis [011] and [$\bar{1}23$] are crystals with a high-temperature SE effect, since this effect is observed in them at temperatures above 373 K. In the [011] orientation, the maximum SE magnitude was 2.8% at a applied strain of 3.5% in the loading–unloading cycle; in the [$\bar{1}23$] orientation, it reached 3.9% at a strain of 4.3% in the loading–unloading cycle (Fig. 2).

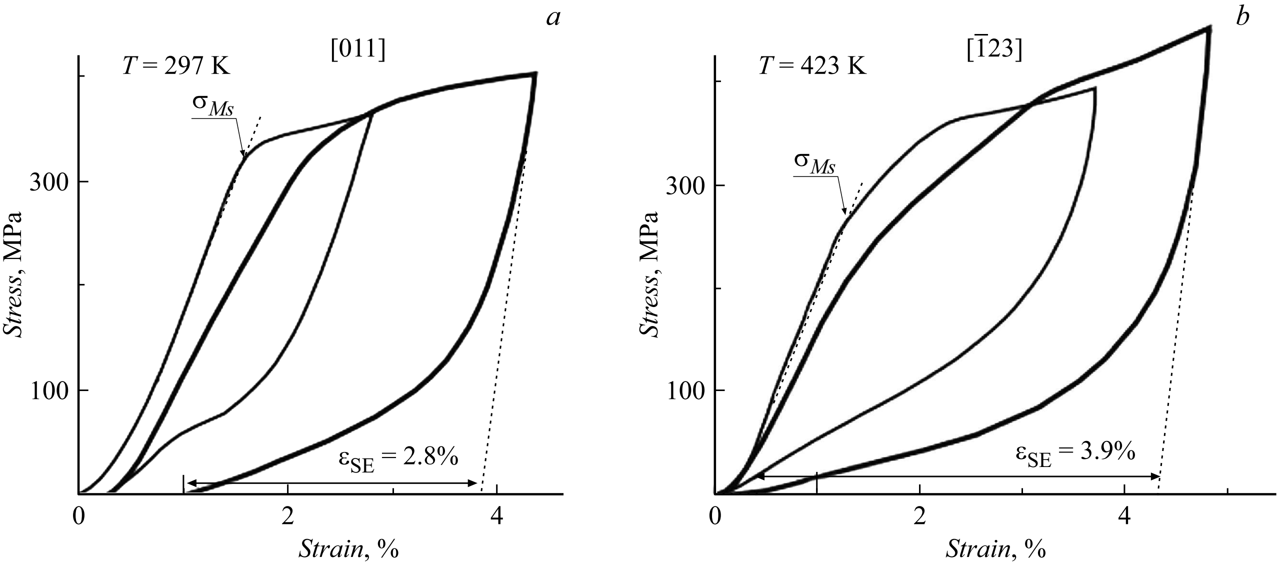

Figure 2. Maximum magnitude of the superelasticity effect in single crystals of the Fe−33Mn−11Al−7Ni−6Cr alloy under compression. *a* — Orientation [011]; *b* — $[\bar{1}23]$.

Figure 3 presents temperature dependences $\sigma_{Ms}(T)$ of stresses of the BCC−FCC MT onset within the temperature range from 203 to 573 K under compression. First, temperature dependence $\sigma_{Ms}(T)$ reveals a strong orientation dependence of stresses σ_{Ms}. For example, $\sigma_{Ms}([\bar{1}11]) = 800\,\mathrm{MPa}$, $\sigma_{Ms}([011]) = 400\,\mathrm{MPa}$, and $\sigma_{Ms}([\bar{1}23]) = 250\,\mathrm{MPa}$ at $T = 243\,\mathrm{K}$. According to relation (1), stresses σ_{Ms} should depend on transformation strain ε_0, since α is proportional to $1/\varepsilon_0$. Indeed, the theoretical values of the transformation strain are

$$\varepsilon_0([\bar{1}11]) = 2\% < \varepsilon_0([011]) = 6\% < \varepsilon_0([\bar{1}23]) = 8.5\%.$$

In accordance with relation (1), this explains why $\sigma_{Ms}([\bar{1}11]) > \sigma_{Ms}([011]) > \sigma_{Ms}([\bar{1}23])$ [1–5]. Stresses σ_{Ms} for single crystals with compression axis $[\bar{1}11]$ remain the highest (1.5−2.5 times higher than stresses σ_{Ms} in orientations [011] and $[\bar{1}23]$) within the entire studied temperature range. Presumably, high stresses σ_{Ms} in orientation $[\bar{1}11]$ turn out to be close to the flow stress of the high-temperature phase. Therefore, the MT in single crystals of this orientation is accompanied by the formation of defects, which leads to a significant increase in dissipated energy ΔG_{diss}, reduction in stored elastic energy ΔG_{el}, and, consequently, suppression of the SE effect [1,2].

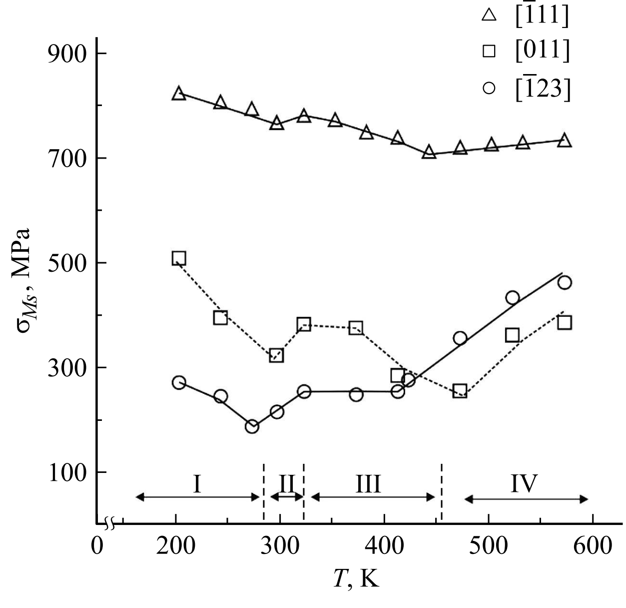

Figure 3. Temperature and orientation dependence of stresses of the onset of the BCC−FCC martensitic transformation in single crystals of the Fe−33Mn−11Al−7Ni−6Cr alloy under compression. Roman numerals indicate temperature ranges.

Second, the $\sigma_{Ms}(T)$ dependence is non-monotonic and has four temperature intervals with different α values. Within the 203−(275−300) K interval (interval I), stresses σ_{Ms} decrease with an increase in temperature, and α has a negative value: $\alpha = -0.28\,\mathrm{MPa/K}$ in orientation $[\bar{1}11]$, $\alpha = -0.98\,\mathrm{MPa/K}$ in orientation [011], and $\alpha = -0.56\,\mathrm{MPa/K}$ in orientation $[\bar{1}23]$. The (275−300)−325 K interval (interval II) is characterized by an increase in stress σ_{Ms} with increasing temperature, and the α value is positive: $\alpha = +0.29\,\mathrm{MPa/K}$ in orientation $[\bar{1}11]$, $\alpha = +1.21\,\mathrm{MPa/K}$ in orientation [011], and $\alpha = +0.68\,\mathrm{MPa/K}$ in orientation $[\bar{1}23]$. Within the 325−(425−475) K interval (interval III), stresses σ_{Ms} either remain unchanged or decrease with increasing temperature, and α becomes equal to zero or has a negative value: $\alpha = -0.28\,\mathrm{MPa/K}$ in orientation $[\bar{1}11]$, $\alpha = -0.62\,\mathrm{MPa/K}$ in orientation [011], and $\alpha = 0\,\mathrm{MPa/K}$ in orientation $[\bar{1}23]$. Similar to temperature interval II, the (425−475)−573 K interval (interval IV) is characterized by an increase in stress

σ_{Ms} with increasing temperature, and the α value is positive: $\alpha = +0.08\,\text{MPa/K}$ in orientation $[\bar{1}11]$, $\alpha = +0.72\,\text{MPa/K}$ in orientation [011], and $\alpha = +0.66$ MPa/K in orientation $[\bar{1}23]$. A similar non-monotonic $\sigma_{Ms}(T)$ dependence has already been observed in [1,2,11].

Thus, temperature intervals I and III have a negative temperature dependence $\sigma_{Ms}(T)$ and a negative value of α in all investigated orientations [3,4]. Therefore, according to relation (1), entropy variation ΔS during the BCC−FCC MT assumes a positive value within these temperature ranges [1–4]. This uncommon behavior (namely, stress σ_{Ms} reduction with an increase in test temperature) is attributable to the influence of magnetic transformations on ΔS and temperature dependence $\Delta S(T)$ [2–4,11].

Thus, experiments with single crystals of the Fe−33Mn−11Al−7Ni−6Cr (at. %) alloy oriented for compression along the $[\bar{1}11]$, $[\bar{1}23]$, and [011] directions have provided the first demonstration that stresses σ_{Ms} of the BCC−FCC MT onset and the SE effect depend on the crystal orientation. The SE effect is observed within a wide temperature range from 203 to 573 K in single crystals with compression axis $[\bar{1}23]$ and [011], and these crystals are the ones with a high-temperature SE effect. Single crystals with compression axis $[\bar{1}11]$ revealed no SE effect. Temperature dependence $\sigma_{Ms}(T)$ is non-monotonic in the studied single crystals of the Fe−33Mn−11Al−7Ni−6Cr alloy: at $T = 203-(275-300)$ and $325-(425-475)$ K, stresses σ_{Ms} decrease with an increase in temperature, and α assumes a negative value.

Funding

This study was supported financially by the Russian Science Foundation, project No. 22-19-00017.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] K. Otsuka, X. Ren, Prog. Mater. Sci., **50** (5), 511 (2005). DOI: 10.1016/j.pmatsci.2004.10.001
[2] K. Otsuka, C.M. Wayman, *Shape memory materials* (Cambridge University Press, Cambridge, 1998).
[3] J. Xia, Y. Noguchi, X. Xu, T. Odaira, Y. Kimura, M. Nagasako, T. Omori, R. Kainuma, Science, **369**, 855 (2020). DOI: 10.1126/science.abc1590
[4] J. Xia, T. Hoshi, X. Xu, T. Omori, R. Kainuma, Shap. Mem. Superelastisity, **7**, 402 (2021). DOI: 1007/s40830-021-00349-8
[5] T. Omori, K. Ando, M. Okano, X. Xu, Y. Tanaka, I. Ohnuma, R. Kainuma, K. Ishida, Science, **333**, 68 (2011). DOI: 10.1126/science.1202232
[6] P. La Roca, A. Baruj, M. Sade, Shap. Mem. Superelastisity, **3**, 37 (2017). DOI: 10.1007/s40830-016-0097-5
[7] L.W. Tseng, J. Ma, S.J. Wang, I. Karaman, Y.I. Chumlyakov, Scripta Mater., **116**, 147 (2016). DOI: 10.1016/j.scriptamat.2016.01.032
[8] C. Zhang, C. Zhu, S. Shin, K. Vecchio, J. Alloys Compd., **768**, 277 (2018). DOI: 10.1016/j.jallcom.2018.07.221
[9] L.W. Tseng, J. Ma, S.J. Wang, I. Karaman, M. Kaya, Z.P. Luo, Y.I. Chumlyakov, Acta Mater., **89**, 374 (2015). DOI: 10.1016/j.actamat.2015.01.009
[10] J.M. Vallejos, M.F. Giordana, C.E. Sobrero, J.A. Malarria, Acta Mater., **179**, 25 (2020). DOI: 10.1016/j.scriptamat.2019.12.038
[11] Yu.I. Chumlyakov, I.V. Kireeva, Z.V. Pobedennaya, I.V. Kuksgauzen, D.A. Kuksgauzen, Mater. Lett., **367**, 136667 (2024). DOI: 10.1016/j.matlet.2024.136667

Translated by D.Safin