The effect of thermal cycling and stress-assistant ageing two-way shape memory effect in [123]-oriented Co40Ni33Al27 single crystals

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Abstract. The effect of thermal cycling through an interval of B2-L10 martensitic transformation (MT) under action of external stress and tensile stress-assistant ageing on the two-way shape memory effect in [123]-oriented Co40Ni33Al27 (at.%) single crystals are investigated. For the first time it is experimentally established that tensile stress-assistant 100 MPa ageing at 573 K for 1 h along [123]-direction of Co40Ni33Al27 single crystals creates the necessary conditions for two-way shape memory effect (TWSME) with the reversible strain up to $\varepsilon=2.4 \pm 0.3\%$ at cooling/heating. The TWSME in quenched [123]-oriented Co40Ni33Al27 single crystals can be induced by thermal cycling through an interval of B2-L10 MT under action of constant external stress 50 MPa with the reversible strain less than 1%.

1. Introduction
In recent years CoNiAl crystals undergoing thermoelastic B2-L10 martensitic transformation (MT) under action of external stress and tensile stress-assistant ageing on the two-way shape memory effect in [123]-oriented Co40Ni33Al27 (at.%) single crystals are investigated. For the first time it is experimentally established that tensile stress-assistant 100 MPa ageing at 573 K for 1 h along [123]-direction of Co40Ni33Al27 single crystals creates the necessary conditions for two-way shape memory effect (TWSME) with the reversible strain up to $\varepsilon=2.4 \pm 0.3\%$ at cooling/heating. The TWSME in quenched [123]-oriented Co40Ni33Al27 single crystals can be induced by thermal cycling through an interval of B2-L10 MT under action of constant external stress 50 MPa with the reversible strain less than 1%.
number of component parts of equipment to wear or break. Thus, the main purpose of this work is clarification of the necessary conditions for TWSME in $[\overline{1}23]$-oriented single crystals of Co$_{40}$Ni$_{33}$Al$_{27}$ (at.%) alloy quenched and aged at 573 K for 1 h.

The high-temperature B2-phase in the quenched Co$_{40}$Ni$_{33}$Al$_{27}$ single crystals involves a large volume fraction ($f > 10\%$) of the $\gamma$-phase (disordered face-centred-cubic structure) compared with Co$_{35}$Ni$_{35}$Al$_{30}$ (volume fraction ($f < 2\%$) of the $\gamma$-phase) [9]. It permits the increasing of ductility of the CoNiAl single crystals due to the presence of the ductile $\gamma$-phase [9] and clarifies the role of $\gamma$-phase in shaping the conditions for the manifestation of TWSME during thermal cycling through an interval of MT under action of stress.

2. Experimental procedures
Single crystals of the Co$_{40}$Ni$_{33}$Al$_{27}$ alloy were grown by the Bridgeman method in an inert gas atmosphere. In order to get clear of the multi-phase state the initial specimens were annealed for 8.5 h at 1613 K and quenched in water at room temperature. Ageing of these single crystals at 573 K for 1 h was performed in a vacuum chamber of the machine for mechanical testing. For stress-assistant ageing the dog-bone shaped flat tensile specimens with the working part dimensions (2.6×1.2×16.0) mm$^3$ in the gauge section was placed in the grips of the machine, and constant load was applied to the sample at $T=473$ K. A low temperature of ageing at $T=573$ K (as compared to $T=673$ K in [5]) was selected for increase of temperature MT and, respectively, working temperatures of TWSME [2]. Prior to testing, the specimens were ground and polished in 200 ml of an electrolytic solution H$_3$PO$_4$+25 ml Cr$_2$O$_3$ at 293 K, $U=20$ V. Mechanical tests were carried out using a specially designed apparatus for measuring SME during cooling/heating under constant stress with output strain-temperature response $\varepsilon(T)$ on the computer. Metallographic observations were carried out with an optical microscope EPITIP-2.

3. Experimental results and discussion
In quenched single crystals one-phase state was not obtained [6,7] and the high-temperature B2-phase contained particles of the $\gamma$-phase of size more than 100 $\mu$m and variants of residual martensite at $T=295$ K (Figure 1). The average volume fraction of the $\gamma$-phase in specimens is $f \approx 8\%$.

Figure 1. Optical metallography quenched $[\overline{1}23]$-oriented Co$_{40}$Ni$_{33}$Al$_{27}$ single crystals.

Figure 2 shows strain-temperature response $\varepsilon(T)$ during cooling/heating of quenched $[\overline{1}23]$-oriented Co$_{40}$Ni$_{33}$Al$_{27}$ single crystals under a constant tensile stress $\sigma$. The sample size and shape is not changed during cooling/heating cycles under the minimum external tensile stress, necessary to secure the specimen in the grips of the machine $|\sigma|=1.6\div3$ MPa (change of size at 3 MPa less than error $\pm 0.3\%$). In this case, the self-accommodation structure of cooling martensite is formed and the TWSME is not observed. During thermal cycling through the temperature interval of MT under action of external tensile stress from 10 to 50 MPa the sample size is changed on cooling.
and completely restored on heating; the SME is then observed. The reversible strain $\varepsilon_{\text{SME}}$ increases with the growth of $|\sigma|$.

**Figure 2.** Strain-temperature response at cooling/heating for quenched [123]-oriented Co$_{40}$Ni$_{33}$Al$_{27}$ single crystals: (a) with applied tensile stress at $|\sigma|=1.6$ from 50 MPa; (b) with applied minimum tensile stresses of $|\sigma|=1.6$ MPa (TWSME).

The maximum value of the reversible strain is $\varepsilon_{\text{SME}}=4.3 \pm 0.3\%$ at 50 MPa, which is close to the theoretical lattice strain of $\varepsilon_0=4.7\%$ in [123] orientation at B2-L1$_0$ MT. In these crystals the linear growth of the martensite start temperature $M_s'$ with the increase in external stress $|\sigma| > 10$ MPa is observed (Figure 3 (a)).

**Figure 3.** The dependence of martensite start temperature $M_s'$ on external tensile stress for quenched (a) and stress-assistant ageing (b) [123]-oriented Co$_{40}$Ni$_{33}$Al$_{27}$ single crystals.
The σ(T) response can be described by the Clausius-Clapeyron relationship [8]:

\[ \frac{d\sigma}{dT} = -\frac{\Delta S^{A-M}}{V_m \cdot \varepsilon_{tr}^{A-M}}, \]

where \( \Delta S^{A-M} \) is the change of entropy associated with the forward transformation, \( \varepsilon_{tr} \) is the transformation strain and \( V_m \) is the molar volume. The coefficient of the σ(T) curve slope is \( \alpha_1 = \frac{d\sigma}{dT} = 2.5 \text{ MPa/K} \) in quenched \([\bar{1}23]\)-oriented Co_{40}Ni_{33}Al_{27} single crystals. TWSME is observed with a small value of reversible strain \( \varepsilon_{TWSME} = 0.6 \text{ (±0.3)\%} \) after thermomechanical training at 40 MPa. The value of TWSME at minimum tensile stresses of 1.6 MPa increases to \( \varepsilon_{TWSME} = 0.9 \text{ (±0.3)\%} \) after thermomechanical training at 50 MPa. In-situ observations of reversible motion of the interface in the loading-unloading cycle show the physical reason for TWSME in quenched crystals. Figure 4 shows that around particles of the γ-phase at room temperature \( T = 293 \text{ K} \) crystals of unoriented \( \text{L}_{10} \)-martensite are formed. Growth of crystals of martensite oriented in accordance with external stresses with the increase of external tensile stresses is observed. After one loading-unloading cycle at \( T = 293 \text{ K} \) in specimens in free state, residual martensite around particles of the γ-phase become oriented in accordance with the applied-stress external stresses in cycle. At the next cooling in free state (without load) the growth of oriented martensite can be generated by oriented residual martensite, creating the necessary conditions for TWSME.

Thus, TWSME in quenched single crystals can be induced by cycle training an interval of MT at 50 MPa with reversible strain of no more 1%.

Figure 2 shows strain-temperature response \( \varepsilon(T) \) during cooling/heating of stress-assisted \([\bar{1}23]\)-oriented Co_{40}Ni_{33}Al_{27} single crystals aged at 100 MPa at 573 K, 1 h, under a constant tensile stress. In stress-assisted aged Co_{40}Ni_{33}Al_{27} single crystals TWSME can be observed without thermomechanical training. The value of the reversible strain at TWSME is \( \varepsilon_{TWSME} = 2.1 \text{ (±0.3)\%} \) at minimum stresses of \( |\sigma| = 1.6 \text{ MPa} \) (Figure 5 (a, b)). Growth of the value of the reversible strain
with the increase of external tensile stress from 1.6 to 15 MPa is observed and temperature $M_s$ slowly increases with coefficient $\alpha_s=0.3$ MPa/K.

The maximum reversible strain of $\varepsilon_{SME}=3.7 \pm 0.3\%$ observed at stress 15 MPa is less than for quenched crystals (Figure 5 (a)). In stress-assisted aged [$\bar{1}23]$-oriented Co$_{40}$Ni$_{33}$Al$_{27}$ single crystals the maximum value of the reversible strain during the development of stress-induced MT is less than for quenched crystals. In heterophase crystals, when calculating the theoretical values of the transformation strain it is necessary to take into account that the particles of second phases do not undergo MT, and, consequently, decrease the volume fraction of the material in which the transformation occurs. This leads to a decrease of the reversible strain compared with the theoretical values of transformation strain and quenched crystals. So, in aged crystals the maximum theoretical values of the transformation strain at B2-L10 MT during the development of stress should be $\varepsilon_0'=\varepsilon_0(1-f)=\varepsilon_{TWSME}$ (f=20% is the average volume fraction of the dispersed particles precipitated during ageing at 573 K, 1 h). The experimental values of the maximum reversible strain in stress-assisted aged crystals are close to the theoretical values of transformation strain at MT.

Training through a temperature interval MT under the action of $|\sigma|=10$ MPa and $|\sigma|=15$ MPa of stress-assisted aged crystals has no material effect on the value of TWSME $\varepsilon_{TWSME} \approx 2.1 - 2.4 \pm 0.3\%$, but the temperature $M_s$ and temperature interval of direct transformation increase (Figure 5 (b)). The value of the reversible strain does not increase after training; therefore the physical reason for TWSME is that these crystals have been attributed to the internal stress fields observed in stress-assistant ageing. This thermomechanical treatment is effective for TWSME.

**Figure 5.** Strain-temperature response at cooling/heating for stress-assistant ageing [$\bar{1}23$]-oriented Co$_{40}$Ni$_{33}$Al$_{27}$ single crystals: (a) with applied tensile stress at $|\sigma|=1.6$ from 15 MPa; (b) with applied minimum tensile stresses of $|\sigma|=1.6$ MPa (TWSME).
4. Conclusions
Thus, the TWSME in quenched [\(\overline{1}23\)]-oriented \(\text{Co}_{40}\text{Ni}_{33}\text{Al}_{27}\) single crystals can be induced by thermal-cycle training an interval of B2-L1\(_0\) MT under action of external stress of 50 MPa with reversible strain of no more 1%. The physical reason for TWSME is that reorientation crystals of residual L1\(_0\)-martensite formed around particles of the \(\gamma\)-phase during the stress-induced MT. For the first time it has been experimentally shown that tensile stress-assistant 100 MPa ageing at 573 K for 1 h along [\(\overline{1}23\)]-direction of \(\text{Co}_{40}\text{Ni}_{33}\text{Al}_{27}\) single crystals creates conditions for TWSME with values of reversible strain up to \(\varepsilon=2.4\, (\pm 0.3)\%\). The physical reason for TWSME in tensile stress-assistant ageing crystals can be attributed to the internal stress fields according to the oriented arrangement of dispersed particles due to summation of the local stress field, arising from the differences in the lattice parameters of the particle and the matrix.

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