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The effect of thermal cycling and stress-assistant ageing two-way shape memory effect in [$\bar{1}$23]-oriented $Co_{40}Ni_{33}Al_{27}$ single crystals

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Abstract. The effect of thermal cycling through an interval of B2-L1_0 martensitic transformation (MT) under action of external stress and tensile stress-assistant ageing on the two-way shape memory effect in [$\bar{1}$23]-oriented $Co_{40}Ni_{33}Al_{27}$ (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 [$\bar{1}$23]-direction of $Co_{40}Ni_{33}Al_{27}$ single crystals creates the necessary conditions for two-way shape memory effect (TWSME) with the reversible strain up to ε=2.4 (±0.3)% at cooling/heating. The TWSME in quenched [$\bar{1}$23]-oriented $Co_{40}Ni_{33}Al_{27}$ single crystals can be induced by thermal cycling through an interval of B2-L1_0 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-L1_0 martensitic transformation (MT) have emerged as new ferromagnetic shape memory alloys. The shape and size of these ferromagnetic materials can be reversed not only by changes in temperature and mechanical stress, but also by applying an external magnetic field. The single crystals of CoNiAl alloys have high-temperature superelasticity at T>373 K, shape memory effect (SME) and a magneto-induced strain of 3.3%, while simultaneously showing action of external stress and magnetic field [1-3]. Fulfilled on aged poly and single crystals of CoNiAl alloys, studies show that precipitation of nanoscale particles leads to a high-strength state and high cyclic stability of functional properties [2-4]. This is very important for operation of devices in cyclic loadings. As shown in [5] the two-way shape memory effect (TWSME) in stress-assistant [$\bar{1}$23]-oriented $Co_{35}Ni_{35}Al_{30}$ single crystals aged at 673 K for 0.5 h can be attributed to the internal stress fields up to $|<\sigma_G>|\sim 75$ MPa by the oriented arrangement of non-equiaxed particles of ε-Co with hcp-lattice of size 20-30 μm [6,7]. In this case the material has a spontaneous recoverable shape change induced during forward and reverse MT at cooling/heating due to the variant selection of cooling-induced martensite by oriented internal stress fields. It is well known that TWSME can be induced by stress-assisted ageing, special thermomechanical treatment and/or training through a temperature interval of MT under constant stress, which generate oriented internal stress fields [8]. The control of internal stress fields and appearance of TWSME allows expansion of the scope of practical application of CoNiAl single crystals. TWSME can greatly simplify the design of devices, and reduce the 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 [$\bar{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 γ-phase (disordered face-centred-cubic structure) compared with $Co_{35}Ni_{35}Al_{30}$ (volume fraction (f< 2%) of the γ-phase) [9]. It permits the increasing of ductility of the CoNiAl single crystals due to the presence of the ductile γ-phase [9] and clarifies the role of γ-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_3PO_4+25 ml Cr_2O_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 ε(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 γ-phase of size more than 100 μm and variants of residual martensite at T=295 K (Figure 1). The average volume fraction of the γ-phase in specimens is f~8%.

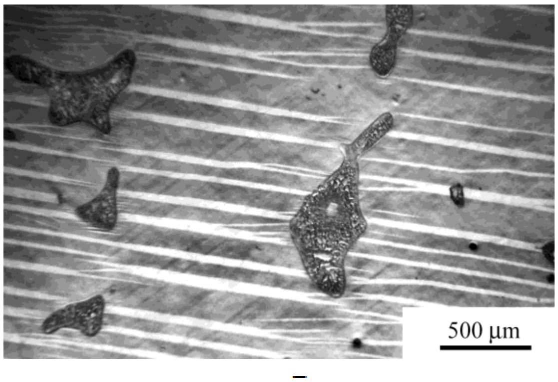

Figure 1. Optical metallography quenched [$\bar{1}$23]-oriented $Co_{40}Ni_{33}Al_{27}$ single crystals.

Figure 2 shows strain-temperature response ε(T) during cooling/heating of quenched [$\bar{1}$23]-oriented $Co_{40}Ni_{33}Al_{27}$ single crystals under a constant tensile stress σ. 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 |σ|=1.6÷3 MPa (change of size at 3 MPa less than error ±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 ε_{SME} increases with the growth of $|\sigma|$.

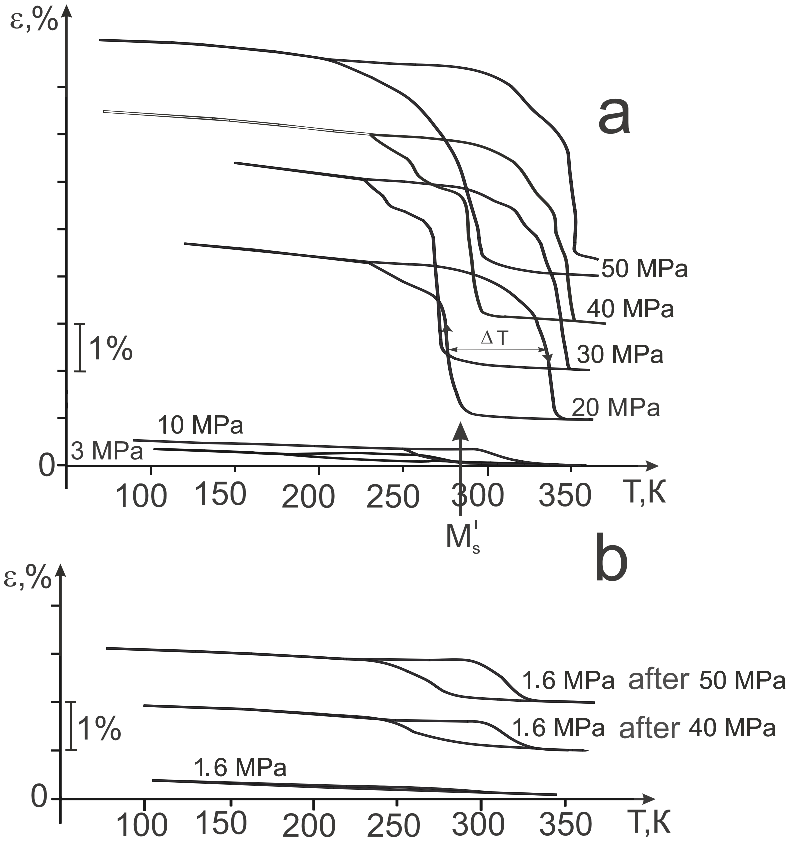

Figure 2. Strain-temperature response at cooling/heating for quenched $[\bar{1}23]$-oriented $Co_{40}Ni_{33}Al_{27}$ single crystals: (a) with applied tensile stress at $|\sigma|$=1.6 from 50 MPa; (b) with applied minimum tensile stresses of $|\sigma|$=1.6 MPa (TWSME).

The maximum value of the reversible strain is ε_{SME}=4.3 (±0.3)% at 50 MPa, which is close to the theoretical lattice strain of ε_0=4.7% in $[\bar{1}23]$ 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)).

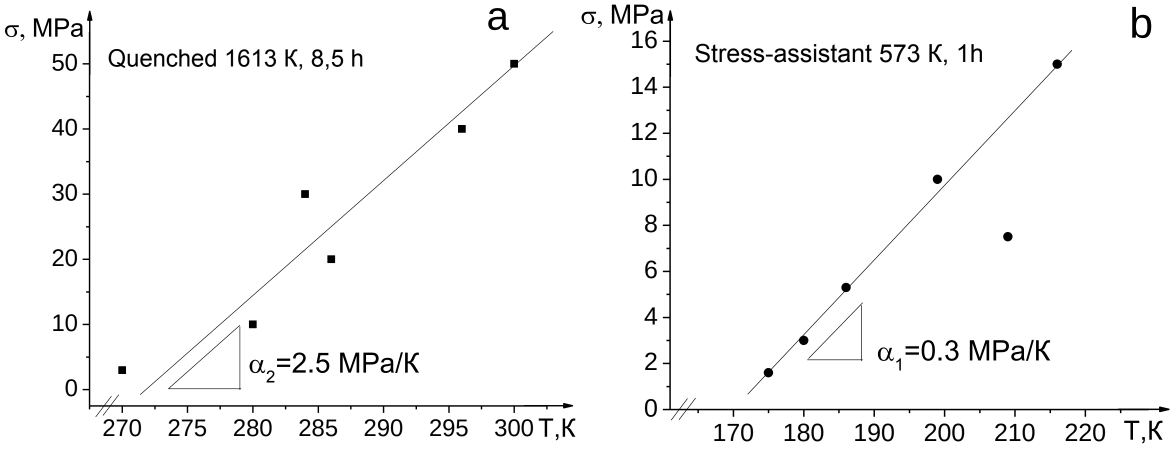

Figure 3. The dependence of martensite start temperature M_s' on external tensile stress for quenched (a) and stress-assistant ageing (b) $[\bar{1}23]$-oriented $Co_{40}Ni_{33}Al_{27}$ single crystals.

The σ(T) response can be described by the Clausius-Clapeyron relationship [8]:

$$\frac{d\sigma}{dT} = -\frac{\Delta S^{A-M}}{\mathrm{V_m} \cdot \varepsilon_{tr}^{A-M}}, \tag{1}$$

where $\Delta S^{A\text{-}M}$ is the change of entropy associated with the forward transformation, ε_{tr} is the transformation strain and V_m is the molar volume. The coefficient of the σ(T) curve slope is $\alpha_1=d|\sigma|/dT=2.5$ 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 $\varepsilon_{TWSME}=0.6$ (±0.3)% after thermomechanical training at 40 MPa. The value of TWSME at minimum tensile stresses of 1.6 MPa increases to $\varepsilon_{TWSME}=0.9$ (±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 K crystals of unoriented $L1_0$-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 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.

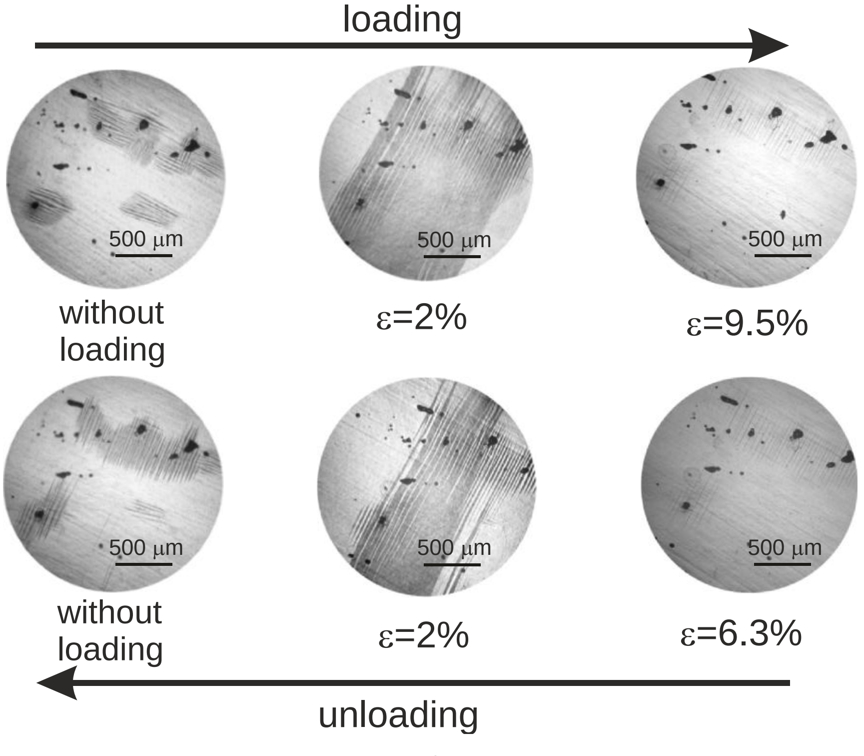

Figure 4. Optical metallography of quenched CoNiAl single crystals.

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 ε(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 $\varepsilon_{TWSME}=2.1$ (±0.3)% at minimum stresses of $|\sigma|=1.6$ 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 α_2=0.3 MPa/K.

The maximum reversible strain of ε_{SME}=3.7 (±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 $\varepsilon_0'=\varepsilon_0(1-f)$=3.8% (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 ε_{TWSME} ≈2.1-2.4 (±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.

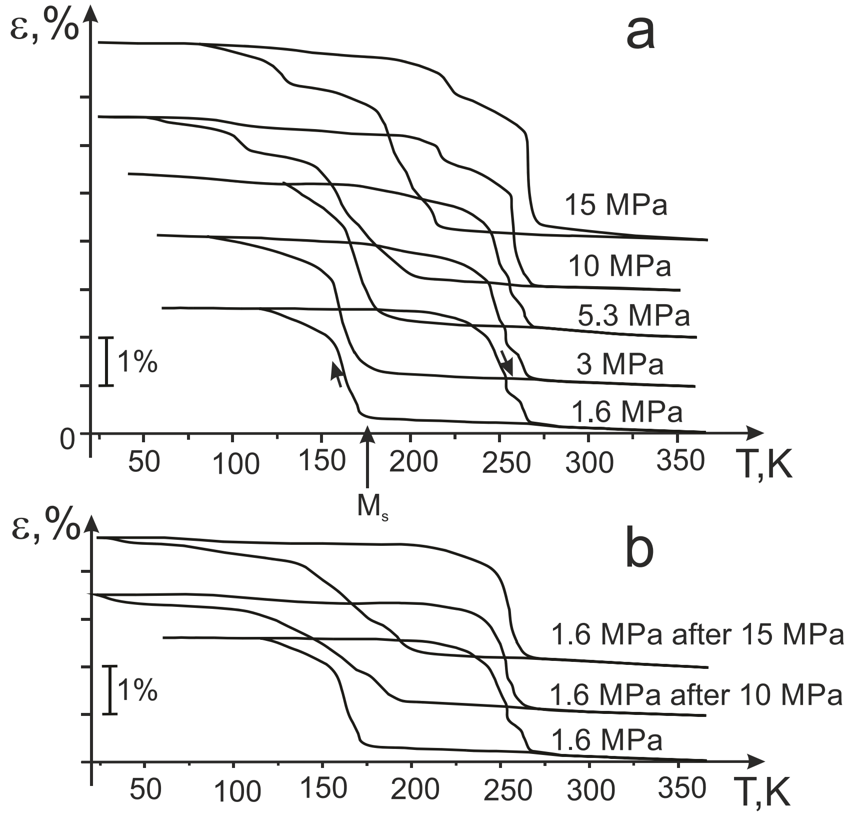

Figure 5. Strain-temperature response at cooling/heating for stress-assistant ageing $[\bar{1}23]$-oriented $Co_{40}Ni_{33}Al_{27}$ single crystals: (a) with applied tensile stress at $|\sigma|$=1.6 from 15 MPa; (b) with applied minimum tensile stresses of $|\sigma|$=1.6 MPa (TWSME).

4. Conclusions

Thus, the TWSME in quenched [$\bar{1}$23]-oriented $Co_{40}Ni_{33}Al_{27}$ 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 γ-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 [$\bar{1}$23]-direction of $Co_{40}Ni_{33}Al_{27}$ single crystals creates conditions for TWSME with values of reversible strain up to ε=2.4 (±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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