Shape memory effect and superelasticity in single crystals of iron-based alloys

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Abstract. It was demonstrated that in single crystals of disordered iron-based (Fe-28%Ni-17%Co-11.5%Al-2.5%X (at. %) (X = Ti, Ta, Ti + Ta) alloys, which undergoing γ-α' thermoelastic martensitic transformation (γ – fcc – face-centered cubic lattice, α' – bct – body-centered tetragonal lattice), the precipitation of ordered γ'-phase particles at aged at 973 K for 0.5 h and 7 h results in the shape memory effect and superelasticity. It was experimentally discovered, that the both mechanical and functional properties – the shape memory effect and superelasticity – can be controlled by changing the chemical composition, the size and the volume fraction of dispersed particles of γ'-phase.

1. Introduction

It is well known that the shape memory effect (SME) and superelasticity (SE) related to reversible thermoelastic martensitic transformations (MT). In turn, reversible thermoelastic MT at cooling/heating without stress and under stress usually occur in the alloys with atomic-ordered structure [1, 2]. And the alloys with disordered structure as a rule show non-thermoelastic MT. In disordered iron-based alloys such as FeMnSi, FeNiCoTi, FeMnNiAl, FePt, FeNiCoAlTa thermoelastic MT result from the precipitation of dispersed γ'-phase particles with L1$_2$ structure, which themselves not be transformed [3-5]. These materials, as it is demonstrated in several studies, possess recoverable transformation strain up to 2-13 %, and therefore have a great interest from the point of view of their practical use, primarily due to the low cost of the material and its treatment as compared with NiTi. The analysis of data, contained in [4, 6, 7], shows that not only the precipitation of ordered γ'-phase but also its chemical composition resulting in thermoelastic γ-α' MT in iron-based alloys by controlling the stability and strength of the phase at γ-α' MT.

By now there are no studies on how the chemical composition, size and volume fraction of dispersed γ'-phase particles influence on mechanical and functional properties of disordered iron-based single crystals. Therefore this work contains the investigation results of the influence of the chemical composition, size and volume fraction of dispersed γ'-phase particles on mechanical and functional properties (SME and SE) in new ferromagnetic single crystals alloys such as Fe-28%Ni-17%Co-11.5%Al-2.5%X (at. %) (X = Ti, Ta, Ti + Ta). In single crystals FeNiCoAlX (X = Ti, Ta, Ti + Ta) alloys the change of chemical composition of γ'-phase particles was achieved by the change of the fifth element, while maintaining of atomic concentration of alloy. The chemical elements Ti and Ta were selected for alloying first of all because Ti is lighter than Ta and has a larger diffusion mobility that

leads to a more uniform distribution of the Ti atoms in the melting of the alloy and crystal growth than Ta does. Thus, it can lead to increased plasticity of crystals with Ti as compared with Ta [8]. Secondly, Ta is heavier than Ti, and therefore, can more effectively increase the particle strength and the stress level in the high temperature phase. Thirdly, in complex-alloyed crystals when the fifth element is defined as a combination of the elements X = Ti + Ta, the particle strength may depend on the aging time at the same aging temperature and this can lead to a difference in the stress level in the high-temperature phase and the stress-induced γ-α' MT [9-11]. γ'-phase particles have a chemical composition $(FeNiCo)_3(AlTi)$, $(FeNiCo)_3(AlTa)$ and $(FeNiCo)_3(AlTiTa)$, respectively, for FeNiCoAlTi, FeNiCoAlTa and FeNiCoAlTiTa [4, 10]. For this work the crystals with [001] orientation were selected, because the maximum lattice strain $\varepsilon_0 = 8.7$ % can be achieved only in this orientation under tension for γ-α' MT [4].

2. Materials and discussion of the results

Single crystals of iron-alloys Fe-28%Ni-17%Co-11.5%Al-2.5%X (at. %) (X = Ti, Ta, Ti + Ta) were grown using the Bridgeman technique in inert gas atmosphere. The single crystals after growth was homogenized at T = 1550 K for 6 h under an inert gas atmosphere, followed by water quenching. The orientation of the crystals was determined by diffractometer DRON-3. Samples for tension along the [001] orientation were cut on electro-discharge machine. SME was measured using a specially designed device when cooling/heating at different levels of external stresses. Mechanical properties of the crystals were examined by the Instron at the temperature interval from 77 K to 525 K at a deformation rate of $4 \cdot 10^{-4}$ c^{-1}. The samples were aged at T = 973 K for 0.5 h (FeNiCoAlTi – crystal 1, FeNiCoAlTa – crystal 2, FeNiCoAlTiTa – crystal 3) and for 7 h (FeNiCoAlTi – crystal 4, FeNiCoAlTa – crystal 5, FeNiCoAlTiTa – crystal 6) in inert gas atmosphere, followed by water quenching. The temperatures of γ-α' MT were determined from change of the temperature dependence of the electrical resistivity ρ(T). In crystals 1-4 the γ-α' MT temperatures are lower than the temperature of liquid nitrogen. In crystals 5 the start temperature of γ-α' MT under cooling $M_s = 125$ K, and the end temperature of reverse transformation under heating $A_f = 200$ K, in crystals 6 − $M_s = 195$ K and $A_f = 220$ K.

Figure 1 shows the results of a study of value of SME at cooling/heating under constant tensile stress for all the investigated crystals. It is evident that in crystals one-step γ-α' MT occurs, which is irreversible in crystals 1-3 aged at 973 K for 0.5 h (Figure 1, a-c) and reversible in crystals 4-6 aged at 973 K for 7 h (Figure 1, d-f).

In crystals 1-3 with applied maximum external stress the maximum value of transformation strain, ε_{SME}, does not achieve the theoretical values of lattice deformation $\varepsilon_0 = 8.7$ % for tension in [001]-orientation crystals with the γ-α' MT [11]. Thus, in crystals 2 the $\varepsilon_{SME} = 3$ % at σ = 575 MPa, and in crystals 1 and 3 the $\varepsilon_{SME} = 2.4$ %, respectively at σ = 600 MPa and 450 MPa. The theoretical values are not achieved due to the crystals destruction under external stress, respectively, σ > 600 MPa in crystals 1, σ > 575 MPa in crystals 2, σ > 450 MPa in crystals 3. And as in crystals 1-3 when heated up to 350-400 K the temperature A_f under stress is not achieved due to the limitation of device of heating to high temperatures, it can be assumed that γ-α' MT in crystals 1-3 aged at 973 K for 0.5 h is characterized by a wide thermal hysteresis under stress ΔT > 150 K. In crystals 4, aged at 973 K for 7 hours, the maximum value of the transformation strain − $\varepsilon_{SME} = 7.8$ % at σ = 375 MPa, and it is close to the theoretical value of the lattice deformation $\varepsilon_0 = 8.7$ % at tension of [001]-orientation crystals with the γ-α' MT [11]. In crystals 5 and 6, aged at 973 K for 7 hours, the maximum value of ε_{SME} does not achieve theoretical values of lattice deformation ε_0: in crystals 5 − $\varepsilon_{SME} = 4.2$ % at σ = 125 MPa; in crystals 6 − $\varepsilon_{SME} = 2.4$ % at σ = 250 MPa. By increasing the external applied stresses crystals are destructed: crystals 4 at σ > 375 MPa, crystals 5 at σ > 125 MPa, crystals 6 at σ > 250 MPa. Thermal hysteresis ΔT under stress for crystals 4, 5 and 6 is respectively 75 K, 60 K and 90 K. It should be noted that when increasing aging time at a given temperature of aging from 0.5 hour to 7 hours, the externally applied stress to achieve maximum transformation strain decreases, that is associated with an increase in M_s temperature by increasing the aging time [12, 13].
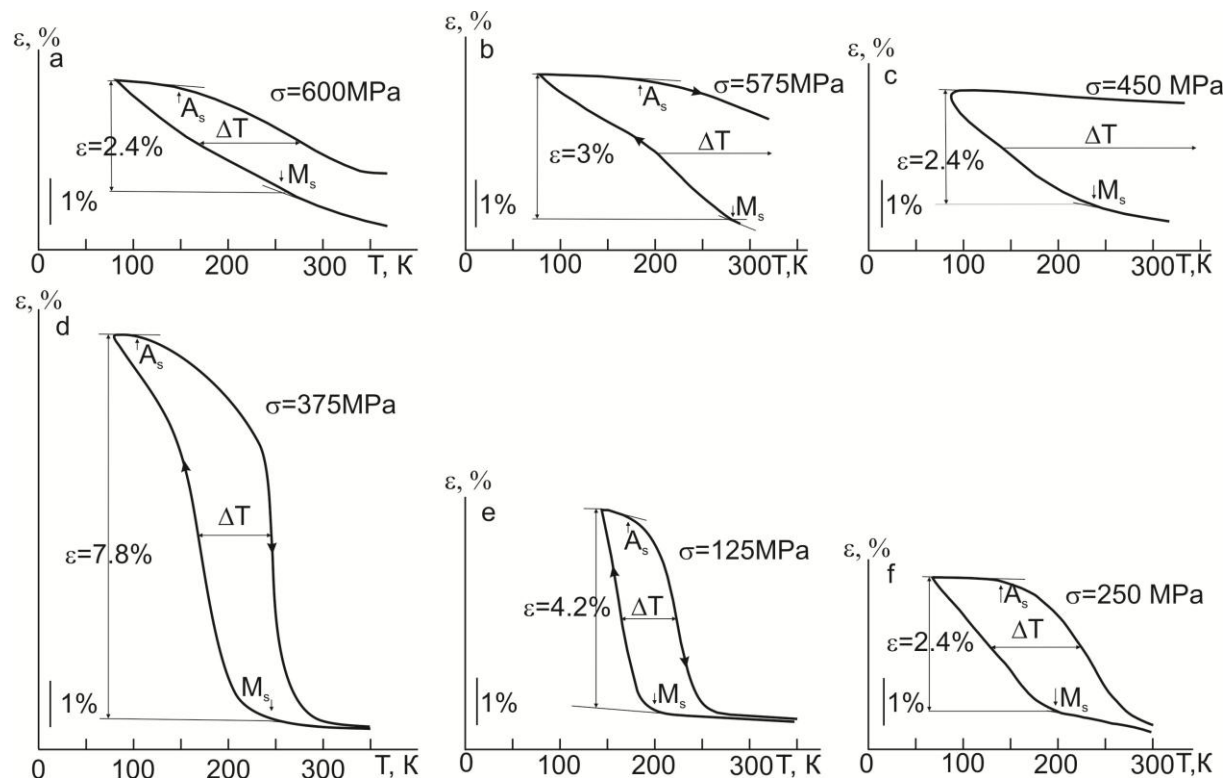
Figure 1. The value of the shape memory effect under constant tensile stress for the [001]-oriented single crystals, aged at T = 973 K, 0.5 hour: a – FeNiCoAlTi, b – FeNiCoAlTa, c – FeNiCoAlTiTa; 7 hours: d – FeNiCoAlTi, e – FeNiCoAlTa, f – FeNiCoAlTiTa.

Figure 2 shows the results of research of SE in depending on the aging time, the test temperature, the value of applied strain in the cycle. In crystals 1-3 according to dependence $\rho(T)$ the γ-α' temperatures are lower than the temperature of liquid nitrogen. At T = 77 K, as can be seen from Figure 2, the SE is observed only in the crystals 2, aged at 973 K for 0.5 h. At the maximum applied strain ε_{ap} = 14.3 % the reversible strain ε_{SE} = 10.8 %, and in size it exceeds value of the lattice deformation ε_0 = 8.7 % at tensile for crystals oriented along the [001] direction with γ-α' MT [11]. Loop SE is characterized by extensive stress hysteresis $\Delta\sigma$ = 290 MPa which is defined as the difference stresses required for direct and reverse martensitic transformation during deformation at half the deformation in cycle. In crystals 1 and 3 at T = 77 K the perfect SE loop is not observed. At the total applied strain 3.4 % and 7.9 %, respectively, in crystals 1 and 3 reversible strain is equal 1 %. This difference in the temperature for appearance of SE at T = 77 K is connected with the difference in temperature M_s, and in the crystals 2 M_s is much lower than in the crystals 1 and 3, apparently.

In crystals 4-6, aged at 973 K, 7 hours, the temperature A_f of γ-α' MT on the data of depending $\rho(T)$ is higher than the temperature of liquid nitrogen and at T > 77 K in these crystals perfect SE loop is observed. In crystals 4 maximum value of SE ε_{SE} = 6 % (Figure 2, d), and in crystals 5 and 6 value of SE ε_{SE} = 4.3-4.5 % (Figure 2, e, f). The value of stress hysteresis $\Delta\sigma$ in the crystals 4-6 is the same and equal to 170 MPa (Figure 2, d-f).

Thus, it is experimentally established that in the [001] single crystals of FeNiCoAlX (X = Ti, Ta, Ti + Ta) alloys thermoelastic γ-α' MT with SME and SE is implemented. Values of ε_{SME}, ε_{SE}, $\Delta\sigma$ depend not only on the size and volume fraction of γ'-phase particles, but also on their composition, and in FeNiCoAlTiTa crystals value of SME and SE is less than in FeNiCoAlTi crystals.
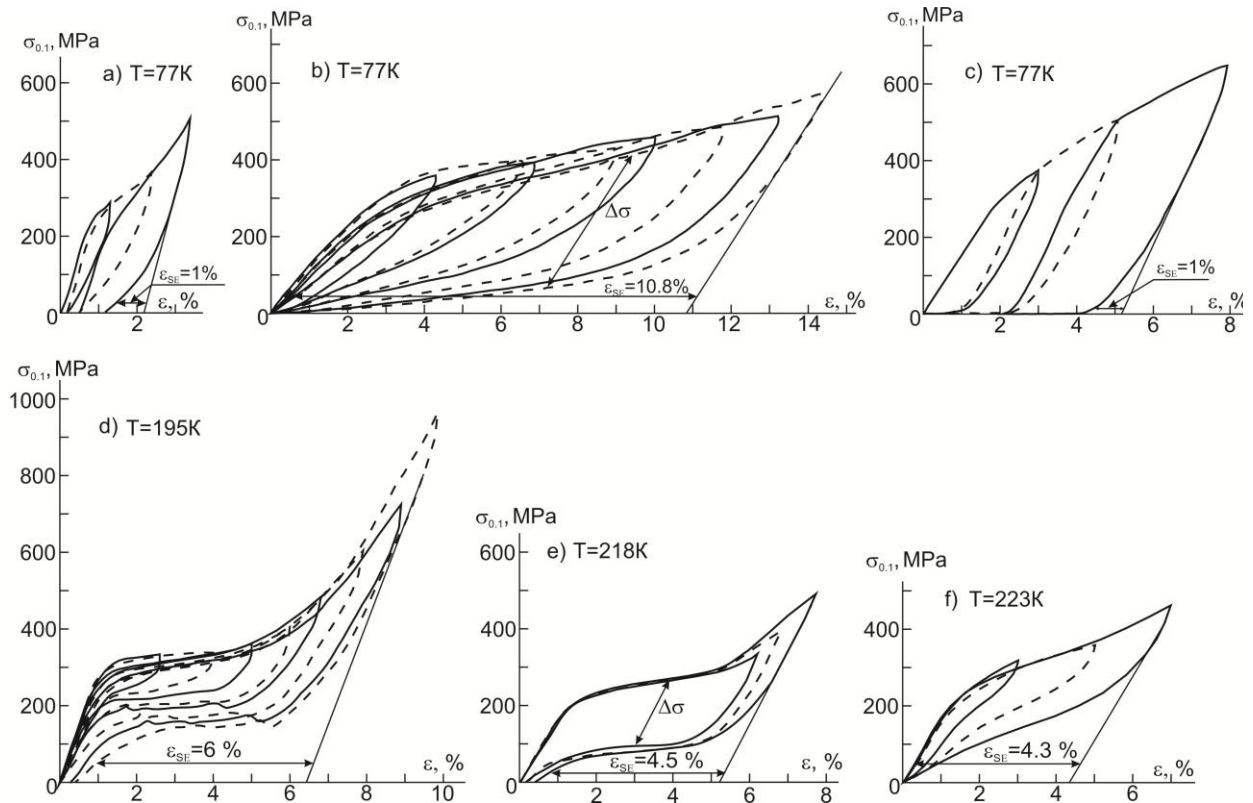
Figure 2. The superelasticity in the [001]-oriented single crystals, aged at T = 973 K, 0.5 hour: a – FeNiCoAlTi, b – FeNiCoAlTa, c – FeNiCoAlTiTa; 7 hours: d – FeNiCoAlTi, e – FeNiCoAlTa, f – FeNiCoAlTiTa.

Diffusion mobility of elements Ti and Ta is different, and the coefficients of diffusion of these elements in iron are in the following sequence $D_{Ti} > D_{Ta}$. Different diffusion mobility of elements Ti and Ta can has impact the processes of formation of the particles in FeNiCoAlTiTa alloy, on their atomic structure at the same aging conditions (temperature and aging time) compared with FeNiCoAlTi and FeNiCoAlTa alloys, and this may affect in the level of strength properties of high-temperature phase, and respectively, on the development of thermoelastic stress-induced γ-α' MT [11].

Electron microscopy studies of the structure of crystals after aging at 973 K for 0.5 h and 7 h show that upon aging for 0.5 hour and 7 hours in crystals FeNiCoAlX (X = Ti, Ta, Ti + Ta) there is precipitation of γ'-phase particles with atomic ordered by type $L1_2$ structure and size of 3-10 nm. The volume fraction of the particles is 15-20 %. Effect of change of the chemical composition on the structure of γ'-phase particles at aging is not established yet and requires further investigation.

In Figure 3 the temperature dependence of axial stresses $\sigma_{0.1}$ for [001]-oriented single crystals FeNiCoAlX (X = Ti, Ta, Ti + Ta), aged at 973 K for 0.5 hour and 7 hours in the temperature range of T = 77-523 K under tensile deformation is presented.

It is clear that for all the crystals FeNiCoAlX (X = Ti, Ta, Ti + Ta), aged at 973 K for 0.5 hour and 7 hours, the dependence $\sigma_{0.1}(T)$ has a characteristic view for alloys experiencing stress-induced MT, and is observed two stages. In the first stage in the temperature range 77 K < T < M_d with increasing test temperature the stresses of $\sigma_{0.1}$ is increased, which is described by the Clausius-Clapeyron relation:

$$\frac{d\sigma_{0.1}}{dT} = -\frac{\Delta H}{\varepsilon_0 T_0} = -\frac{\Delta S}{\varepsilon_0} \, , \tag{1}$$

here ΔH and ΔS – respectively enthalpy and entropy change at γ-α' MT; ε_0 – transformation strain; T_0 – temperature of chemical equilibrium of γ- and α'-phases.
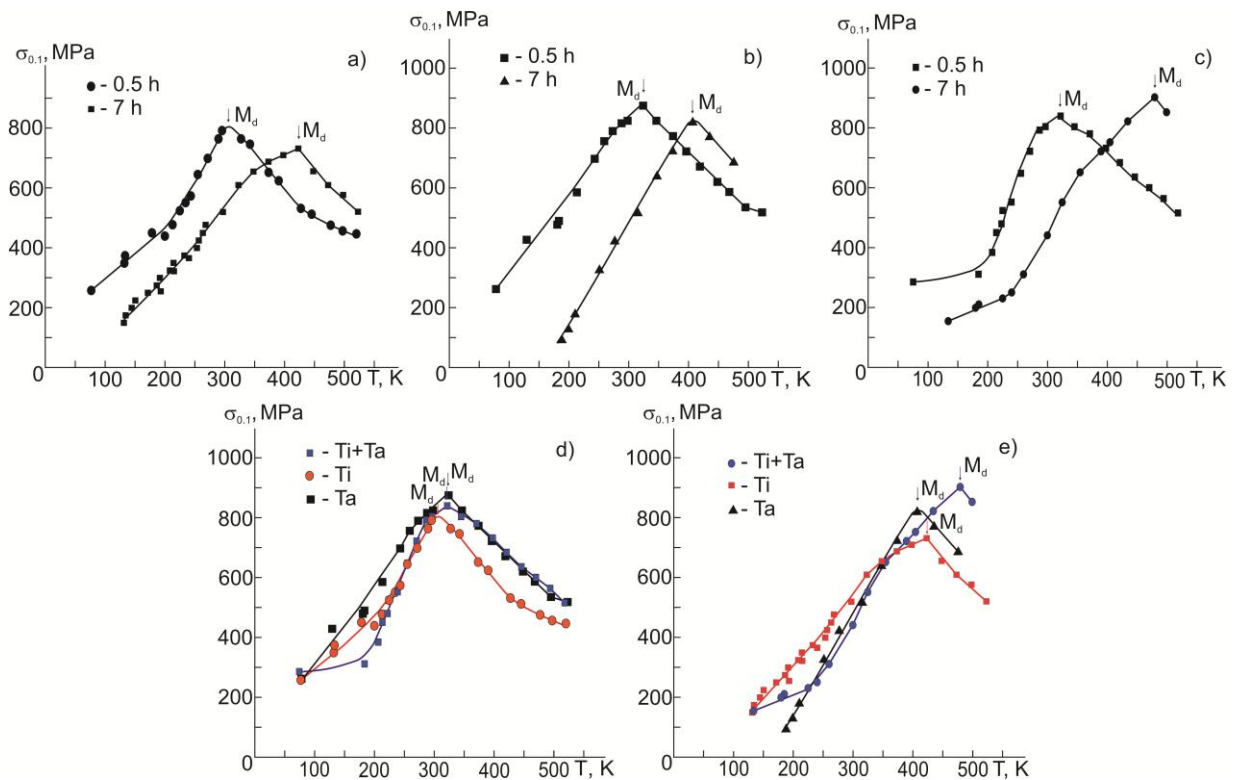
Figure 3. The temperature dependence of the axial stresses $\sigma_{0.1}$ for single crystals oriented along the [001] direction, at tensile deformation: a) FeNiCoAlTi, b) FeNiCoAlTa, c) FeNiCoAlTiTa, d) aging at 973 K, 0.5 hour, e) the aging at 973 K, 7 hours.

The second stage at $T > M_d$ associated with plastic deformation of high-temperature phase and it is characterized by the normal temperature dependence of the yield stress is typical for fcc materials [14]. Data analysis of $\sigma_{0.1}(T)$ in Figure 3 shows that, firstly, in all crystals FeNiCoAlX (X = Ti, Ta, Ti + Ta) with increasing aging time parallel shift of $\sigma_{0.1}(T)$ curves observed and, the less the aging time the lower direct temperature of γ-α' MT. The value of $\alpha = d\sigma/dT$ at this weakly dependent on aging time and is in the range 2.5-3.2 MPa/K (Figure 3, a-c). Secondly, at same time of the aging, stress level of the high temperature phase at $T = M_d$ depends on the chemical composition of the γ'-phase particles. Thus, upon aging at 973 K for 0.5 hour $\sigma_{0.1}^{Ti}(M_d) < \sigma_{0.1}^{Ti + Ta}(M_d) < \sigma_{0.1}^{Ta}(M_d)$, and at aging at 973 K 7 hours $\sigma_{0.1}^{Ti}(M_d) < \sigma_{0.1}^{Ta}(M_d) < \sigma_{0.1}^{Ti + Ta}(M_d)$ (Figure 3, d, e). Therefore, in complex-alloyed crystals FeNiCoAlTiTa, level of strength properties of high-temperature phase determined by the chemical composition of γ'-phase particles, which is determined by the aging time. Due to the different diffusion mobility of Ti and Ta ($D_{Ti} > D_{Ta}$) γ'-phase particle in complex-alloyed crystals FeNiCoAlTiTa can has different concentration of Ta and respectively characterized by different strength, which has an impact on the level strength properties of high-temperature phase [9]. For a small aging time – 0.5 hour, when the γ'-phase particles are less durable, stresses level of high-temperature phase at $T = M_d$ in crystals with Ti and Ti + Ta is close, and the γ-α' MT is characterized by close regularities: large thermal and stress hysteresis under stress and lack of SE at $T = 77$ K as compared with crystals Ta. At aging during 7 hours the γ'-phase particles in Ti + Ta crystals the richer Ta than at aging for 0.5 hour, and so should be stronger. This is qualitatively confirmed by that in FeNiCoAlTiTa crystals, aged at 973 K for 7 hours, the stresses level of high-temperature phase is greater, and energy dissipation at γ-α' MT, which is determined by the value of stress hysteresis $\Delta\sigma$, and the value of transformation strain in the experiments studying of SME and SE is smaller than in the crystals of Ti and Ta.

3. Conclusion
In the [001]-oriented single crystals of disordered iron-based Fe-28%Ni-17%Co-11.5%Al-2.5%X (at. %) (X = Ti, Ta, Ti + Ta) alloys it is shown that the precipitation of ordered γ'-phase particles during the aging at T = 973 K for 0.5 h and 7 h leads to the development of thermoelastic γ-α' MT with SME and SE. It is experimentally discovered that variation of the chemical composition, size and volume fraction of the dispersed γ'-phase particles allows to control both mechanical and functional properties. It is shown that the maximum values of reversible strain in experiments on research of the SE are equal to 10.8 % observed in single crystals of Fe-28%Ni-17%Co-11.5%Al-2.5%Ta (at. %) aged at T = 973 K for 0.5 h that exceed the theoretical values of the lattice deformation of 8.7 % in tension for crystals oriented along the [001] direction with the γ-α' MT [4]. Maximum value of SME ε_{SME} = 7.8 % observed in the Fe-28%Ni-17%Co-11.5%Al-2.5%Ti (at. %) crystal after aging at T = 973 K for 7 h, which is close to the theoretical values of the lattice deformation of 8.7 %. Found that in complex-alloyed crystals Fe-28%Ni-17%Co-11.5%Al-2.5%TiTa (at. %), the strength properties of the high-temperature phase, the development of stress-induced γ-α' MT, value of the thermal ΔT and stress $\Delta\sigma$ hysteresis determined by chemical composition of the γ'-phase particles.

Acknowledgements

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