Shape Memory Effect and Superelasticity in [001] Single Crystals of FeNiCoAlNb(B) Alloys

# Shape Memory Effect and Superelasticity in [001] Single Crystals of FeNiCoAlNb(B) Alloys

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**Abstract.** In given paper presents data research of influence of boron on the functional properties - the shape memory effect and superelasticity in the [001] single crystals FeNiCoAlNb(B) alloys aged at 973 K for 5 hours. On the [001] single crystals FeNiCoAlNbB at aging at T = 973 K for 5 hour, it is shown, that boron leads to decrease the start $M_s$ temperature of γ-α' martensitic transformation on cooling, to the development of γ-α' stress-induced martensitic transformation at higher stress at one test temperature and to increase of thermal $\Delta T$ and stress $\Delta\sigma$ hysteresis is compared to [001] crystals without boron.

## 1. Introduction

In recent years, interest to the ferromagnetic iron-based alloys with thermoelastic γ-α' martensitic transformations (MT) have been increasing. Firstly, iron-based alloys are more durable, have low cost, better ductility and weldability as compared to known TiNi alloys [1]. Secondly, a large shape change can obtain not only under the influence of temperature, the stress, but also the magnetic field [2]. It is known [3-14], that in order to γ-α'-MT in FeNiCoTi, FeNiCoAlTa, FeNiCoAlTi iron-based alloys was thermoelastic the precipitation of disperse particles of ordered γ'-phase is necessary. In the polycrystals at precipitation of γ'-phase particles in grain body occur precipitation of β-phase on the grain boundaries, which leads to brittle fracture and does not allow to get the shape memory effect (SME) and superelasticity (SE). In the polycrystals FeNiCoAlTa, FeNiCoAlTi alloys to suppress the precipitation of β-phase additionally alloyed with boron [5, 6]. In the present work, was set a problem to investigate the effect of boron on the value of the SME, SE, the value of stress hysteresis $\Delta\sigma$ in single crystals of Fe-28Ni-17Co-11.5Al-2.5Nb(0.05 B) (at.%) alloys at aging at T = 973 K for 5 hours at tensile deformation. The single crystals of these alloys in the absence of grain boundaries in a pure form will allow to reveal a difference in development of stress-induced γ-α'-MT in crystals on iron-based alloys with boron and without boron. For study the γ-α' stress-induced martensitic transformation were selected single crystals oriented along the [001] direction, because in given orientation the theoretical value the strain lattice $\varepsilon_0 = 8.7$ % has a maximum value for γ-α'-MT at tensile deformation [5].

## 2. Materials and discussion of the results

Single crystals of Fe-28Ni-17Co-11.5Al-2.5Nb(0.05 B) (at.%) alloy were grown by the Bridgman's method in inert gas atmosphere. Single crystal was confirmed by the X-ray method and optical microscopy of the etched crystal surface. Test samples were cut on electro-discharge machine in dog-bone-shaped with dimensions working part 1.5×12×3 mm. The single crystals after growth were

homogenized at T = 1550 K 6 hours in an inert gas atmosphere followed by the quenching in water. The aging of single crystals FeNiCoAlNb(B) alloy was performed at a temperature T = 973 K for 5 hours in a helium atmosphere. Mechanical properties of crystals tested on Instron testing machine in a temperature range from 77 to 525 K with a strain rate of $4 \cdot 10^{-4}$ $s^{-1}$. The shape memory effect was determined on a specially designed installation at cooling/heating under different levels of external stresses. The study of crystal surfaces after removal of the load was conducted by the digital optical microscope VHX-2000.

Investigation of temperature dependence of electrical resistance $\rho(T)$ for the single crystal FeNiCoAlNb(B) alloys after quenched and aging at T = 973 K, 5 hours is showed that both in the quenched state and after aging at 973 K for 5 hours on $\rho(T)$ curve the specific stage for development of MT in these alloys is not observed and $\rho$ is independent of temperature [4, 10]. For determination the possibility of development of reversible stress-induced $\gamma$-$\alpha'$-MT in single crystals of FeNiCoAlNb(B) alloys the investigated of the temperature dependence of the critical stresses $\sigma_{cr}$, the SME at cooling/heating under a constant load and the SE.

The figure 1 shows the results of studies of the temperature dependence of the critical stresses $\sigma_{cr}$ at tension for [001]-oriented single crystals of FeNiCoAlNb(B) alloys after quenching and aging at T = 973 K.
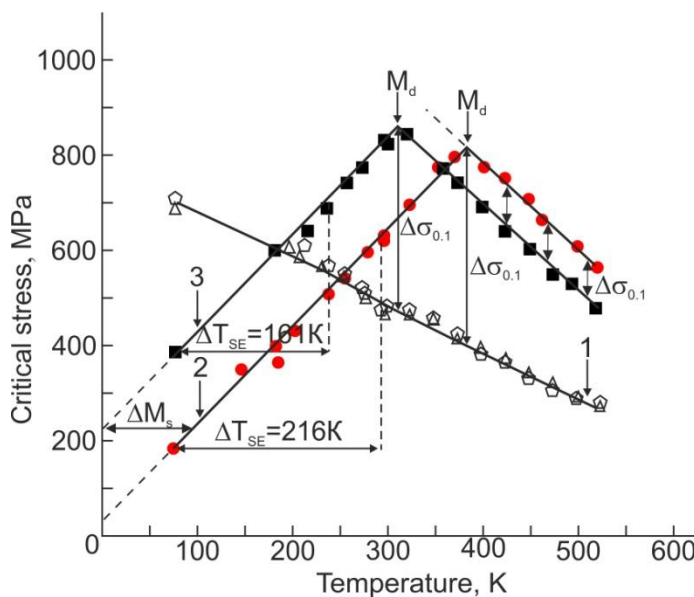


**Figure 1.** Temperature dependence of critical stresses $\sigma_{cr}$ for [001] single crystals FeNiCoAlNb(B) alloys at tensile deformation: curve 1 – single-phase state after quenching; the curve 2 – the FeNiCoAlNb crystals, aged at T = 973 K, 5 hours; curve 3 – FeNiCoAlNbB crystals, aged at T = 973 K, 5 hours.

It is seen that in the single-phase state after quenching the $\sigma_{cr}(T)$ curve has a normal temperature dependence characteristic for single- and polycrystals of FCC-alloys − with increasing test temperature the $\sigma_{cr}$ was decreased (figure 1, curve 1) [15]. It is qualitative confirmation that stress-induced $\gamma$-$\alpha'$ martensitic transformation in single-phase crystals in the temperature range T = 77 − 550 K does not develop at stresses near the yield stress, which also agrees with the experimental data obtained at the study of temperature dependence of $\rho(T)$. Under alloying with boron up to 0.05 at.% the $\sigma_{cr}$ in single crystals of FeNiCoAlNbB alloy are equal $\sigma_{cr}$ in single crystals of FeNiCoAlNb alloy (figure 1, curve 1). Therefore, at the concentration of boron equal to 0.05 atm. % the hardening effect of it is zero. The temperature dependence $\sigma_{cr}(T)$ at aging at T = 973 K, 5 hours differs from $\sigma_{cr}(T)$ for a

single-phase state and has the kind characteristic for alloys which undergoes stress-induced MT [7], namely, on the temperature dependence $\sigma_{cr}(T)$ in single crystals FeNiCoAlNb(B) alloy in the T = 77 − 550 K temperature range two stages is observed. In the first stage at 77 K < T < $M_d$ ($M_d$ is the temperature at which the yield stress level of high-temperature phase is equal to the critical stress level for stress-induced martensite) $\sigma_{cr}$ increases with increasing temperature, which is described by the Clausius-Clapeyron relation [7]:

$$\frac{d\sigma_{cr}}{dT} = -\frac{\Delta H}{\epsilon_0 T_0}.$$  (1)

Where $\Delta H$ − enthalpy change at $\gamma$-$\alpha'$-MT; $\epsilon_0$ − transformation strain which depends of crystal orientation; $T_0$ − chemical phase-equilibrium temperature. The second stage is characterized by a normal temperature dependence $\sigma_{cr}(T)$, which is usually observed under the slip deformation in FCC-crystals.

Analysis of the data presented in fig. 1 shows firstly that upon alloying boron $\sigma_{cr}(T)$ dependence of the parallel shifted to the area of the lower temperatures. The $\sigma_{cr}(T)$ curves which are extrapolated on $\sigma_{cr} = 0$ show that the values of $M_s$ in crystals with a boron and without boron lie less than the temperature of liquid nitrogen and in crystals with boron the $M_s$ and $M_d$ temperatures are respectively on 90 K and 80 K lower than in crystals without boron. Consequently, the boron leads to stabilization of high-temperature phase. The value of $\alpha = d\sigma_{cr}/dT$ in crystals with boron and without boron prove to be same and equal $\alpha_{Nb} = \alpha_{NbB} = 2.05$ MPa/K.

Secondly, at alloying by boron the stress of high-temperature phase at T > $M_d$ less on 50 MPa than in crystals without boron. Since the solid-solution hardening by boron at low concentrations in single crystals FeNiCoAlNb(B) is equal to zero (figure 1, curve 1), the hardening of high-temperature phases of crystals with boron and without boron at aging T = 973K 5 hours can determine in pure form at the test temperature, which above $M_d$ temperature, for example, 400 K, by the ratio [16, 17]:

In crystals without boron

$$\Delta\sigma_{cr} = \sigma_{cr}(Nb) - \sigma_{cr}(WQ)$$  (2a)

In crystals with boron

$$\Delta\sigma_{cr} = \sigma_{cr}(NbB) - \sigma_{cr}(WQ).$$  (2b)

Where $\sigma_{cr}(WQ)$ − stress of high-temperature phase of crystals without boron and with boron after quenching while $\sigma_{cr}(Nb)$ and $\sigma_{cr}(NbB)$ the stress in crystals without boron and with boron after aging at 973 K 5 h, respectively. Hardening of the high-temperature phase in crystals with boron and without boron after aging at 973 K for 5 hour at test temperature T = 400 K are equal, respectively, 380 and 415 MPa and in crystals without boron above on 35 MPa. Investigation of the crystals structure with boron and without boron after aging at T = 973 K, 10 hours shows that in crystals with boron the size and the volume fraction of $\gamma'$-phase particles is less than in crystals with boron. Therefore, boron slows the aging process and at one aging at T = 973 K, 5 hours crystals are characterized by different structure (size and volume fraction of particles in crystals with boron and boron are different). And because level of the strength properties of high-temperature phase determined by the size and volume fraction of particles, according to the relation [16, 17]:

$$\sigma_{cr} = 3 \cdot G \cdot E^{3/2} \cdot (f \cdot r / b)^{1/2},$$  (3)

here G − the shear modulus of the high-temperature phase, E = $\Delta a/a$ − parameter misfit of lattice of high-temperature the phase and the particles ($\Delta a = a_m - a_{par}$), f − volume fraction of particle, r − radius of the particle, b − a module of the Burgers vector of a slip dislocation, that in the crystals without boron the level of stress to must be larger than in crystals with the boron as observed experimentally.

It has been experimentally established that after aging at T = 973 K, 5 hours in crystals FeNiCoAlNb(B) alloys the $\gamma$-$\alpha'$-MT is thermoelastic and SME and SE are observed.

Figure 2 presents the results of the research of the SME in the experiment during cooling/heating under external tensile stresses for the [001]-crystals FeNiCoAlNb(B) alloys, aged at 973 K, 5 hour. From the figure 2 it can be seen that in crystals FeNiCoAlNb(B) under load is realized one-stage $\gamma$-$\alpha'$-

MT. In crystals FeNiCoAlNb $\gamma$-$\alpha'$-MT is reversible, thus SME is observed. At the external stresses $\sigma$ = 400 MPa the maximum value of reversible strain $\varepsilon_{SME}$ = 2.5 % is observed, which is 3 times less than the theoretically calculated values of the lattice strain $\varepsilon_0$ = 8.7 % for the [001]-crystals at the $\gamma$-$\alpha'$-MT [5].
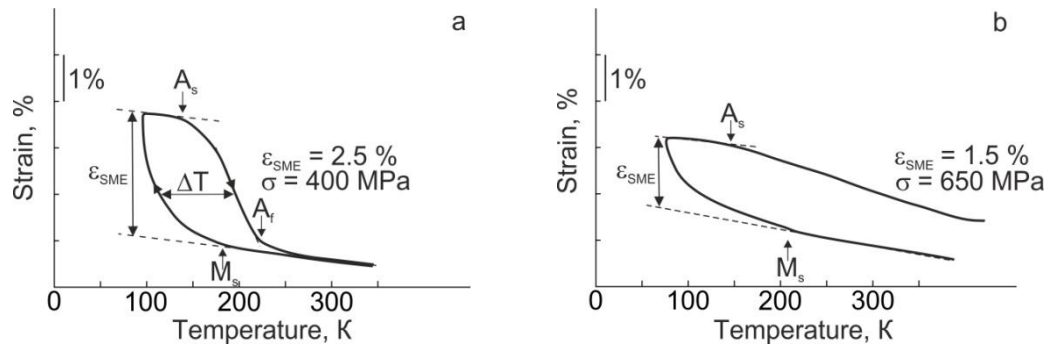


**Figure 2.** The shape memory effect $\varepsilon_{SME}$ at constant external tensile stresses in the [001]-oriented single crystals aged at 973 K 5 hour: a) FeNiCoAlNb; b) FeNiCoAlNbB.

This is due to the fact that the crystal at stress $\sigma$ = 400 MPa is destroyed before it reaches the theoretical value $\varepsilon_0$. The value of thermal hysteresis under load $\Delta T$ = 75 K (fig. 2a). In FeNiCoAlNbB crystals the $\varepsilon_{SME}$ = 1.5 % is observed when the external stresses $\sigma$ = 600 MPa and in this case $\gamma$-$\alpha'$-MT is irreversible. The irreversible strain is disappears when the load is removed with followed the keeping the sample at room temperature, sample does not restore its original dimensions and the residual martensite on the surface is observed (fig. 3). Given that the form of temperature hysteresis loop not closed, that finish temperature of reverse MT $A_f$ under load $\sigma$ during heating is not achieved and can assume that the hysteresis in single crystals FeNiCoAlNbB alloy $\Delta T$ > 200 K.
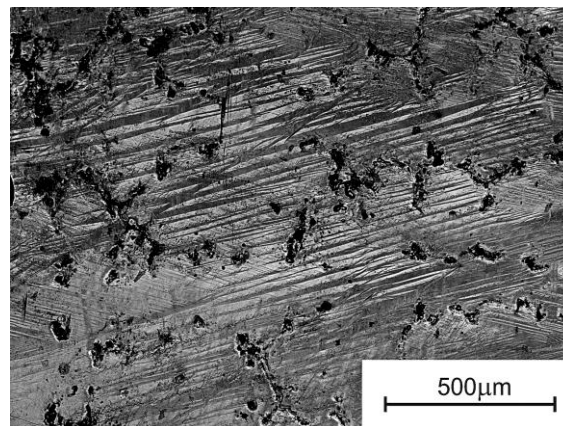


**Figure 3.** The residual $\alpha'$-martensite on the surface of [001]-oriented FeNiCoAlNbB crystals aged at 973 K for 5 hour at the load is removed $\sigma$ = 650 MPa.

It has been experimentally established that at aging 973 K 5 hour in single crystals FeNiCoAlNb SE is observed from T = 77 K to 293 K, and its temperature range is equals $\Delta T_{SE}$ = 216 K, and in single crystals FeNiCoAlNbB SE is observed from T = 77 K to 238 K and $\Delta T_{SE}$ = 161 K (Fig. 1).

Figure 4 shows the results of studies SE in the [001]-single crystals FeNiCoAlNb(B) alloys aged at 973 K for 5 hours at tensile deformation, depending on a given strain value in cycle at T = 77 K.

Visible that in [001] crystals FeNiCoAlNb(B) the value of SE $\varepsilon_{SE}$ = 5 % and it is limited due to brittle fracture of crystals at strain $\varepsilon_{SE}$ > 5 %. The value of stress hysteresis $\Delta\sigma$, which is defined as the difference of stress required for the forward and reverse MT on half of deformation cycle, in the

crystal FeNiCoAlNb equals 50 MPa and in crystals FeNiCoAlNb (B) is 4 times more. It should also be noted that in crystals without boron the γ-α'-MT starts at the stress $\sigma_{cr}$ = 180 MPa and «σ-ε» curve is characterized by two stages: the first stage with the strain-hardening coefficient $\Theta = d\sigma/d\varepsilon$ close to zero with ε = 3.5 % and the second stage with ε > 3.5 % with high Θ = 1330 MPa. In crystals with a boron the γ-α'-MT develops at $\sigma_{cr}$ = 380 MPa, which is 2 times higher than in the crystals without boron and on «σ-ε» curve the one stage with Θ = 3600 MPa is observed.
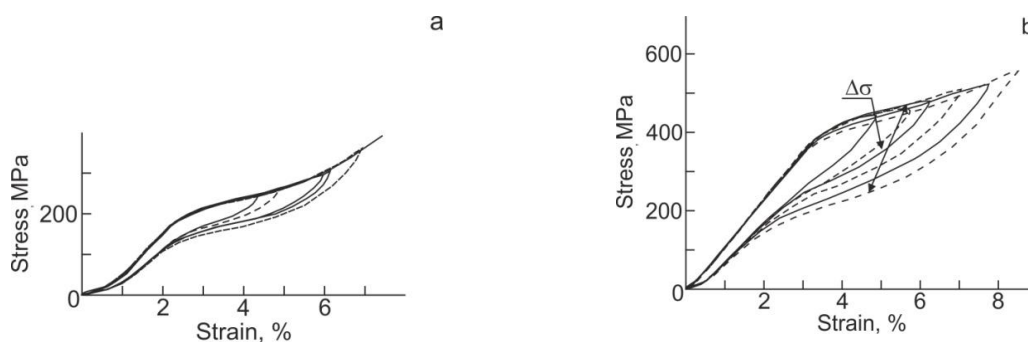


**Figure 4.** «σ-ε» curves for [001]-oriented single crystals of alloy aged at 973 K for 5 hours under tension: a) FeNiCoAlNb and b) FeNiCoAlNbB; test temperature T = 77 K.

Thus, it has been experimentally established that in the [001] single crystals of FeNiCoAlNb(B) aged at 973 K for 5 hours the thermoelastic stress-induced γ-α' MT with the SME and SE is observed, and their value, temperature range of SE $\Delta T_{SE}$, the value of stress hysteresis Δσ in single crystals are found to depend on the presence of boron in crystals of FeNiCoAlNb alloy with the same aging time T = 973 K 5 hour. From [11, 13] it follows that the level of stress of high-temperature phase determines the value $\Delta T_{SE}$ and Δσ: the high strength properties of high-temperature phase the more $T_{SE}$ and the less Δσ. In crystals FeNiCoAlNb aged at 973 K for 5 hours the level of the strength properties of high-temperature phase is higher than it in crystals FeNiCoAlNbB (figure 1), in consequence the temperature range of SE is greater, and Δσ is less. In FeNiCoAlNbB crystals the boron leads to a significant decrease of $M_s$ compared to crystals without boron and at temperature T = 77 K the γ-α'-MT is developing at the stress which is 2 times less stress at T = $M_d$. This leads to the fact that the stress-induced γ-α' martensitic transformation is followed by processes of local plastic current and this is cause an increase Δσ in crystal with boron compared to crystals without boron.

**3. Conclusion**
1.   It has been established experimentally that in the single crystals of Fe-28%Ni-17%Co-11.5%Al-2.5%Nb (at.%) with boron and without boron aged at 973 K for 5 hours the γ-α' thermoelastic martensitic transformation with the shape memory effect and superelasticity at tensile deformation is develops.

2.     It was shown that the boron in single-crystal Fe-28%Ni-17%Co-11.5%Al-2.5%Nb alloy leads to reduction the temperature $M_s$, to reduction the temperature range of superelasticity $\Delta T_{SE}$ and to increase the value of stress hysteresis Δσ compared to the crystal without boron under the same conditions of aging (temperature and time aging).

3.     It has been found out that the temperature dependence for the start of a stress-induced γ-α'-martensitic transformation in tension in the [001] single crystals of Fe-28%Ni-17%Co-11.5%Al-2.5%Nb alloy aged at 973 K for 5 hours with boron and without boron is described by the Clausius-Clapeyron equation. It is shown that boron is leaded to a parallel shift of the curves $\sigma_{cr}(T)$ in area the low-temperature of test without changing the value of $\alpha = d\sigma_{0.1}(T)/dT$, which is associated with decreasing temperature $M_s$.

## Acknowledgements

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