Orientation dependence of the shape memory effect and superelasticity in ferromagnetic $Co_{49}Ni_{21}Ga_{30}$ single crystals with γ'-phase particles

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Orientation dependence of the shape memory effect and superelasticity in ferromagnetic $Co_{49}Ni_{21}Ga_{30}$ single crystals with γ'-phase particles

I V Kuksgauzen[1], I V Kireeva[1], Y I Chumlyakov[1] and H Maier[2]
[1]National research Tomsk State University, Tomsk, Russia
[2]Institut für Werkstoffkunde, Leibniz Universität Hannover, Garbsen, Germany

E-mail: irbas@sibmail.com

Abstract. This paper reports on the orientation dependence of the shape memory effect and superelasticity in [001] and $[\bar{1}23]$ single-phase and aged at 623K, 1 hour single crystals of ferromagnetic $Co_{49}Ni_{21}Ga_{30}$ (at.%) alloy with B2-$L1_0$ martensitic transformation. It was demonstrated that in single-phase crystals the values of reversible strain and the values of thermal and stress hysteresis depend on the crystal orientation. Precipitation of γ'-phase particles reduces the value of the shape memory effect and superelasticity and reduces their orientation dependence, increases the thermal and stress hysteresis in comparison with single-phase crystals.

1. Introduction

Currently, the ordered CoNiGa alloys with B2-$L1_0$ thermoelastic martensitic transformation (MT) (B2 – ordered phase based on volume-centered cubic lattice, $L1_0$ – tetragonal martensite based on a face-centered tetragonal lattice) are promising ferromagnetic alloys with high strength and good ductility [1-8]. In CoNiGa crystals, firstly, a high stress level of the high-temperature phase can be achieved by choosing the orientation. It is known [9] that in alloys with B2 structure the dislocation slip takes place along the <100> direction on {110}, {100} slip planes. Under tension/compression deformation the [001] crystals are characterized by high stresses level of B2-phase because of the Schmid factor for operating slip systems is zero in contrast to other orientations, in which Schmid factors for these systems are high. Therefore crystals oriented along the [001] direction should show a wider temperature interval of stress-induced MT compared with other crystal orientations. Secondly, a high stress level of high-temperature phase in CoNiGa alloy can be achieved by precipitation of γ'-phase particles (γ'-phase – an ordered face-centered cubic with $L1_2$ structure) [1-4, 10]. Precipitation of γ'-phase particles will allow to expand the temperature interval of superelasticity (SE) not only in the [001]-oriented crystals, but also in other orientations, result from increased stress levels of high-temperature phase and suppression of local plastic flow processes during the formation of martensite crystals under stress and to receive alloys with high-temperature of SE, a manifestation which will not depend on the crystal orientation. To date there have been no systematic investigations of the simultaneous influence of the crystal orientation and dispersed γ'-phase particles on the functional properties of single-crystal of $Co_{49}Ni_{21}Ga_{30}$ alloys. Therefore, in this paper presented the results of investigations on the effect of crystal orientation and γ'-phase particles on the value of shape memory effect (SME), ε_{SME}, and SE, ε_{SE}, thermal ΔT^{σ} and stress $\Delta\sigma$ hysteresis under stress, the temperature interval of SE, ΔT_{SE}, in [001]- and $[\bar{1}23]$-oriented single crystals of $Co_{49}Ni_{21}Ga_{30}$ (at.%) alloy at compression. This choice of orientation was defined as follows: firstly, the crystals are characterized by different values of the lattice deformation: in [001]-oriented single crystals under compression ε_0=4.5%, and $[\bar{1}23]$-oriented single crystals – ε_0=3.2%, for this reason, in the work is supposed to receive orientation dependence of the value of reversible strain on the experiments of SME and SE. Secondly, in the [001]-oriented single crystals the contribution of detwinning strain of $L1_0$-martensite, ε_{detw}, to the total lattice deformation at B2-$L1_0$ MT is zero, and in the $[\bar{1}23]$-oriented single crystals $L1_0$-martensite detwinning takes place and the associated strain of ε_{detw}=0.8% [6] . This choice of orientations will allow not only to trace the influence of orientation on the functional properties due to different values of ε_0, but also reveal the influence of $L1_0$-martensite detwinning on energy dissipation processes.

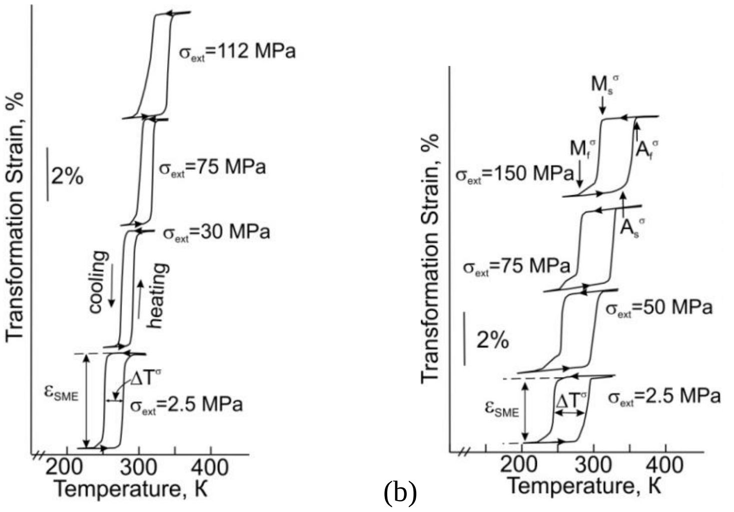
2. Materials and methods

Single cryslals of $Co_{49}Ni_{21}Ga_{30}$ (at.%) alloy were grown by the Bridgman technique in inert gas atmosphere. Samples for compression tests were in parallelepiped form in size of 3x3x6 mm^3 with the compression axis oriented along the [001] and $[\bar{1}23]$ directions. For single-phase state the samples were kept at T=1430 K for 30 minutes in quartz tubes in inert gas atmosphere followed by water quenching. To precipitate the nanometric dispersed γ'-phase particles selected low temperature aging at 623 K for 1 hour. After this aging the γ'-phase particles are spherical of size d=5 nm, and the volume fraction of f=15% [1]. Shape memory effect was measured using a specially designed installation when cooling/heating at different levels of external stresses. SE effect of single crystals were examined by the Instron 5969 at the temperature interval from 273 K to 623 K under compression. MT temperatures in free state were determined by differential scanning calorimetry (DSC). In the single-phase crystals peaks of direct and reverse transformation are observed by the DSC method and B2-$L1_0$ MT is characterized by low thermal hysteresis: $\Delta T = A_f - M_s = 296-272 = 24K$ (M_s – start temperature of the forward MT on cooling; A_f – the finish temperature of the reverse MT on heating). At precipitation of nanometric γ'-phase particles after aging at T=623 K, 1h the MT temperatures shifted to lower temperatures: M_s=165K, A_f=274K, and the thermal hysteresis $\Delta T = A_f - M_s$=109K increased in 4.5 times in comparison with single-phase crystals without γ'-phase particles.

3. Results and discussion

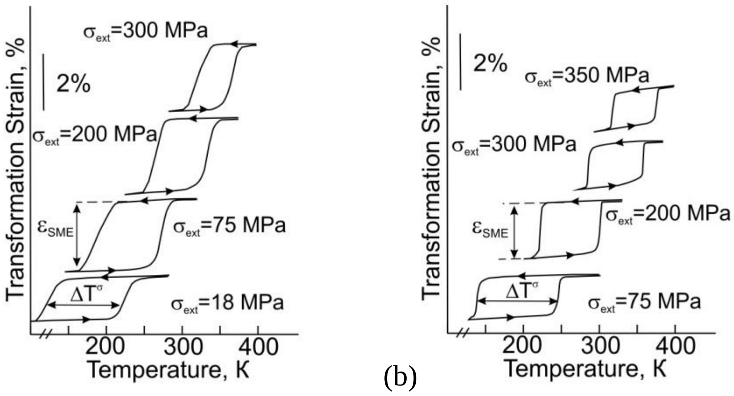
Figures 1 and 2 presents the results of a study of SME recorded during cooling/heating experiments under different external stresses from 2.5 MPa to 350 MPa for crystals oriented along the [001] and $[\bar{1}23]$ directions in a single-phase state and after aging at 623K, 1 h. Such experiments allow us to determine the B2-$L1_0$ MT temperatures, the value of thermal hysteresis, ΔT^{σ}, and transformation strain, ε_{SME}, depending on external applied stresses.

It is seen that in single-phase crystals oriented along the [001] and $[\bar{1}23]$ directions one-stage B2-$L1_0$ MT is realized, which is fully reversible by heating and thus SME is observed. The value of SME in single-phase crystals depends on the crystal orientation. Thus, in crystals oriented along the [001] direction, at σ_{ext}=2.5 MPa the $\varepsilon_{SME}^{[001]}$=3.5%, and this value is close to theoretically calculated value of the lattice deformation ε_0=4.5% for a given crystal orientation at B2-$L1_0$ MT [6]. Consequently, even at minimal external stresses of σ_{ext}=2.5 MPa in single-phase crystals oriented along the [001] direction, occurs the destruction of the self-accommodated $L1_0$-martensite microstructure and growth oriented twinned $L1_0$-martensite [4]. In [001]-oriented single crystals at σ_{ext}=20 MPa reaches a maximum reversible strain $\varepsilon_{SME}^{[001]}$=4.2%, which is equal to the value of ε_0=4.5% for a given orientation of the crystals at B2-$L1_0$ MT [6]. With increasing σ_{ext}>60 MPa the value of $\varepsilon_{SME}^{[001]}$ decreases slightly. In crystals oriented along the $[\bar{1}23]$ direction at σ_{ext}=2.5 MPa $\varepsilon_{SME}^{[\bar{1}23]}$=2.5% and this value is close to theoretically calculated value of the lattice deformation ε_0=3.2% for the $[\bar{1}23]$ crystals at B2-$L1_0$ MT as well [6]. This means that in $[\bar{1}23]$ crystals at the minimum stress at σ_{ext}=2.5 MPa self-accommodated $L1_0$-martensite structure is destroyed and there is a growth oriented $L1_0$-martensite containing no twins as the value of ε_{SME}=2.5% at σ_{ext}=2.5 MPa exceeds value of ε_0=ε_{CVP}=2.4% (the contribution of detwinning strain of L1_0-martensite in [$\bar{1}$23] crystals at B2-L1_0-MT is 0.8% [6]). When σ_{ext}>20 MPa the ε_{SME}=2.9% reaches a maximum value close to the value of ε_0 for a given orientation of the crystals at B2-L1_0 MT [6] and with the increasing of σ_{ext} the ε_{SME} remains practically constant. In both crystal orientations with minimal external compressive stresses the start temperature of the forward B2-L1_0 MT on cooling under stress is identical and M_s^σ=263 K. This temperature is close to M_s, that determined by DSC for single-phase crystals in the free state. However, the value of the thermal hysteresis $\Delta T^\sigma=A_f^\sigma-M_s^\sigma$, characterizing the energy dissipation at MT under stress, in [001]-oriented single crystals has smaller value than in [$\bar{1}$23]-oriented single crystals, and in stress interval of σ_{ext}=2.5÷40 MPa decreases from ΔT^σ=27K to ΔT^σ=15K and then remains constant, and in [$\bar{1}$23]-oriented single crystals, on the contrary, increases from ΔT^σ=42K to ΔT^σ=55K (figure 1). In [$\bar{1}$23]-oriented crystals with increasing applied external stresses the position of habit plane of L1_0-martensite under detwinning is changed relatively non-detwinning state. This leads to additional internal stresses and energy dissipation under unloading and it associated with the increase of ΔT^σ in the [$\bar{1}$23] crystals. In [001]-oriented single crystals, where the detwinning strain of L1_0-martensite suppressed because of equality to zero Schmid factors, habit plane of L1_0-martensite does not change its position [11], energy dissipation when unloading there is no and ΔT^σ in [001]-oriented single crystals does not increase.



(a) (b)

Figure 1. «σ-T» curves for the [001] (a) and [$\bar{1}$23] (b) single-phase crystals of $Co_{49}Ni_{21}Ga_{30}$ alloy



(a) (b)

Figure 2. «σ-T» curves for the [001] (a) and [$\bar{1}$23] (b) single crystals of $Co_{49}Ni_{21}Ga_{30}$ alloy aged at T=623K for 1 h.

With increasing applied stress levels σ_{ext} in [001]- and $[\bar{1}23]$-oriented single crystals observed the temperature M_s^{σ} rise. With increasing M_s^{σ} the stresses $\sigma_{ext}=\sigma_{cr}$ lay down on the linear relationship (figure. 4), which is described by the Clausius-Clapeyron relation [11]:

$$\frac{d\sigma_{cr}}{dT} = -\frac{\Delta H\rho}{\varepsilon_0 T_0} = -\frac{\Delta S\rho}{\varepsilon_0}, \qquad (1)$$

here ΔH and ΔS – respectively enthalpy and entropy change at B2-$L1_0$ MT; ε_0 – lattice deformation which depends on the crystal orientation; T_0 – temperature of chemical phase equilibrium which may be calculated as $T_0 = 1/2(M_s+A_f)$ and ρ – mass density.

From figure 3 shows that in the single-phase [001] and $[\bar{1}23]$ crystals value of $\alpha=d\sigma_{cr}/dT$ depends on the crystal orientation: $\alpha^{[001]}=1.74$ MPa/K, $\alpha^{[\bar{1}23]}=2.95$ MPa/K. Orientation dependence of $\alpha=d\sigma_{cr}/dT$ is due to the orientation dependence of the $\varepsilon_{SME}=\varepsilon_0$. From (1) that smaller value of $\alpha=d\sigma_{cr}/dT$ should corresponds to larger value of ε_0 and, in contrast, the smaller value of ε_0 should corresponds to larger value $\alpha=d\sigma_{cr}/dT$. This is confirmed experimentally. Thus, in the [001]-oriented single crystal smaller value of $\alpha^{[001]}=1.74$ MPa/K corresponds to a larger value of $\varepsilon_{SME}=4.2\%$, and in the $[\bar{1}23]$-oriented single crystals, in contrast, a larger value of $\alpha^{[\bar{1}23]}=2.95$ MPa/K corresponds to a smaller value of $\varepsilon_{SME}=2.9\%$. At that $\alpha^{[\bar{1}23]}/\alpha^{[001]}=1.7$ ratio and $\varepsilon_{SME}^{[001]}/\varepsilon_{SME}^{[\bar{1}23]}=1.5$ ratio are close to each other in accordance with equation (1).

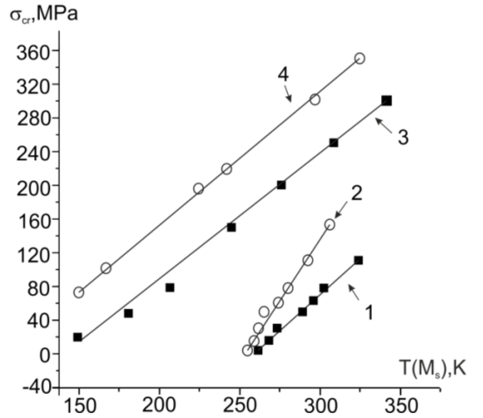


Figure 3. Temperature dependence of stresses σ_{cr} for single-phase (1, 2) and aged at T=623K, 1 h (3, 4) [001]- (1, 3) and $[\bar{1}23]$ - (2, 4) oriented single crystals of $Co_{49}Ni_{21}Ga_{30}$ alloy.

In addition, using the relation (1) can calculate theoretical values of $\alpha=d\sigma_{cr}/dT$ and compare them with the experimental values of $\alpha=d\sigma_{cr}/dT$. Entropy change ΔS, obtained in experiments by DSC on $Co_{49}Ni_{21}Ga_{30}$ single crystals equal 10.0 J/kg K, and the mass density ρ of the $Co_{49}Ni_{21}Ga_{30}$ crystals is equal 8470 kg/m^3 was directly obtained by the measurement of the single crystal [2]. Using the data of ΔS, ρ and experimental values of ε_{SME} for the appropriate orientation were obtained theoretical values of $\alpha=d\sigma_{cr}/dT$: $\alpha^{[001]}=2.02$ MPa/K, a $\alpha^{[\bar{1}23]}=2.9$ MPa/K and these values are close to the experimental obtained values of α for the corresponding orientation.

At precipitation of γ'-phase particles in crystals oriented along the [001] and $[\bar{1}23]$ directions does not change the nature of the MT and one-stage B2-$L1_0$ MT is observed as well as in single-phase crystals, which completely reversible after heating. Consequently, SME is realized. As can be seen from figure 2 at the precipitation of γ'-phase particles the SME under stress at σ_{ext} exceeds of σ_{ext} for single-phase crystals without the particles and the value of SME becomes smaller. Thus, in the [001]-oriented single crystal of $\varepsilon_{SME}=1.5\%$ is observed when $\sigma_{ext}=18$ MPa, and in $[\bar{1}23]$-oriented sungle crystals $\varepsilon_{SME}=1.6\%$ at $\sigma_{ext}=75$ MPa. When $\sigma_{ext}=100$ MPa values of SME are close: $\varepsilon_{SME}[001]=2.2\%\approx\varepsilon_{SME}[\bar{1}23]=1.9\%$ and with increasing of σ_{ext} values of SME vary slightly (Figure 3, b, curves). Therefore, the dispersed γ'-phase particles creates significant resistance to the movement of interphase and twin boundaries. Decrease of ε_{SME} at precipitation of γ'-phase particles may be due to several factors: 1) a decrease in the volume fraction of the matrix, which undergoes MT with precipitation of γ'-phase particles, which do not undergo the MT and 2) difficulties of detwinning deformation of $L1_0$-martensite [12].

At precipitation of γ'-phase particles after aging at T=623K, 1 h in both orientations there is a decline of M_s^σ temperature on ~110K as compared to single-phase state (Figure 1, 2). That also correlated with the data obtained by DSC [1]. At that the value of ΔT^σ is larger than in single-phase crystals and with growth of σ_{ext} in both orientations the value of ΔT^σ is decreased. For example, in [001]-oriented single crystals with γ'-phase particles at minimal σ_{ext}=18 MPa the ΔT^σ=100K and with increasing stress up to σ_{ext}=300 MPa the ΔT^σ is reduced to 50 K. In the [$\bar{1}$23] - oriented single crystal with γ'-phase particles at minimum σ_{ext}=75MPa value of ΔT^σ=110K with increasing of σ_{ext} to 350 MPa the ΔT^σ is reduced by 2 times. As well as in single-phase state in the crystals with particles $\Delta T^\sigma[\bar{1}23]>\Delta T^\sigma[001]$ (figure 2). The physical reason of the increase of ΔT^σ in crystals with particles compared with single-phase crystals without the particles is associated with resistance of particle to movement interphase and twins boundaries, with interaction of martensitic variants (interaction of martensite arising near the particles with stress-induced martensite) and with increasing density of twins martensite as has previously been shown in [1]. When the stress increases selection variant of stress-induced martensite is advantageous and the interaction between martensite variants makes a smaller contribution to the energy dissipation and this may be due to a decrease of ΔT^σ with growth of external applied stress [4].

With an increase in the level of external applied stress σ_{ext} in [001]- and [$\bar{1}$23] - oriented single crystals with γ'-phase particles as well as single-phase crystals the M_s^σ temperature rise is observed and with increasing of M_s^σ the stresses of $\sigma_{ext}=\sigma_{cr}$ are falling on linear dependence. As seen from figure 4 the value of $\alpha=d\sigma_{cr}/dT$ in the crystals with γ'-phase particles becomes smaller than a single-phase state for corresponding orientation and weakly dependent on orientation: $\alpha^{[001]}$=1.49 MPa/K и $\alpha^{[\bar{1}23]}$ =1.55 MPa/K. According to relation (1), when the value of SME decreases the values of $\alpha=d\sigma_{cr}/dT$ must increase and, therefore, must be larger than in single-phase crystal for corresponding orientation. This contradiction of the experimental data with the relation (1) is due to the dependence of the ε_{SME} and ΔT^σ and, accordingly, energy dissipation on the level of externally applied stresses, that by us it was shown in [2]. The weakening of the orientation dependence of $\alpha=d\sigma_{cr}/dT$ in crystals with the γ'-phase particles is due to degeneration orientation dependence of ε_{SME} value and the ratio of $\varepsilon_{SME}^{[001]}/\varepsilon_{SME}^{[\bar{1}23]}$=1.1 is equal to the ratio of $\alpha^{[\bar{1}23]}/\alpha^{[001]}$=1.0.

Experimental studies of the superelastisity in single crystals of $Co_{49}Ni_{21}Ga_{30}$ alloy showed that in [001]-oriented single-phase crystals the SE is observed a wide temperature interval from A_f=283K to 573K, ΔT_{SE}=290K that is associated with the development of reversible stress-induced B2-$L1_0$ MT. Therefore, the studied alloys exhibit high-temperature SE. In [$\bar{1}$23] -oriented single-phase crystals SE is observed in the temperature interval of T=318÷473K and ΔT_{SE}=155K. Precipitation of γ'-phase particles leads to an expansion of temperature interval of SE in both orientations: in [001]-oriented single crystals the SE observed from T=273K to T=623K and $\Delta T_{SE}[001]$=350K and in [$\bar{1}$23] – from T=298K to T=573K and $\Delta T_{SE}[\bar{1}23]$=275K that exceeds the ΔT_{SE} in single-phase crystals for the corresponding orientations. In the crystals oriented along the [$\bar{1}$23] direction SE also has a place at T=573K. Consequently, the precipitation of γ'-phase particles provides a large temperature interval of SE including at high temperature at T>573K, not only in [001]- orientation, but also in other orientations due to increasing the stresses level of high-temperature phase and suppressing local plastic flow processes during stress-induced martensite.

Figure 4 shows the «σ-ε» curves at T=323K for single-phase and aged at T=623K, 1 h [001]- and [$\bar{1}$23] - oriented single crystals at compression. It is seen that the γ'-phase particles influence the development of stress-induced MT. In single-phase crystals value of SE, ε_{SE}, and value of stress hysteresis, Δσ, which is defined as the difference stresses required for direct and reverse MT during deformation at half of SE loop, depend on the crystal orientation: in [001]-oriented single crystals at T=323K ε_{SE}=4.5%, Δσ=25 MPa, and in [$\bar{1}$23]-oriented single crystals at T=323K ε_{SE}=3.2%,

$\Delta\sigma$=73MPa. Precipitation of γ'-phase particles leads to a decrease of ε_{SE}, increase of $\Delta\sigma$ and weakening their orientation dependence: in [001]-oriented single crystals at T=323K ε_{SE}=2.2%, $\Delta\sigma$=90MPa, and in $[\bar{1}23]$-oriented single crystals ε_{SE}=2.1% and $\Delta\sigma$=95MPa. It should be noted that the value of SE equals to the value of SME for corresponding crystals orientation both in single-phase state and with the γ'-phase particles.

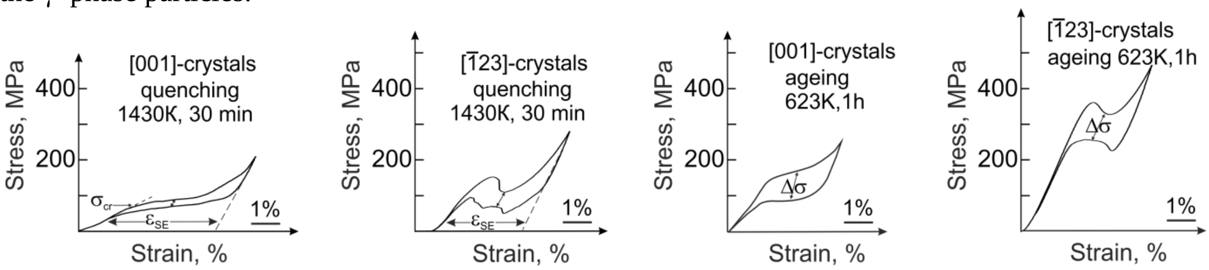


Figure 4. «σ-ε» curves at T=323K for the [001]- and $[\bar{1}23]$- oriented single-phase and aged at T=623K, 1h single crystals of $Co_{49}Ni_{21}Ga_{30}$ alloy.

4. Summary

It was established experimentally that in single-phase $Co_{49}Ni_{21}Ga_{30}$ (at. %) crystals the values of SME and SE, the temperature interval of SE, the values of thermal and stress hysteresis depend on the crystal orientation. In [001]-oriented single-phase crystals the value of SME and SE has a maximum value equal to 4-4.5%. SE is observed over a wide temperature interval ΔT_{SE}=290K and high temperature at T=573K and characterized of narrow stress hysteresis.

Precipitation of γ'-phase particles leads to a decrease values of SME and SE, an increase of the temperature interval of SE, of the values of stress and thermal hysteresis under stress and a weakening them depending on the crystal orientation. It is shown that in crystals with the γ'-phase particles due to changes in the level of external applied stresses can control the value of thermal hysteresis from 100-110K up to 50 K.

It is shown that an increase in strength properties of high-temperature phase due to the γ'-phase precipitate can be obtained the SE over wide temperature interval and at high temperatures not only in the crystal of [001] orientation but in $[\bar{1}23]$ -oriented single crystals.

Acknowledgements

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