Influence of particles on the functional properties of single crystals of high-strength ferromagnetic alloys

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Abstract. Single crystals of the ordered ferromagnetic Co$_{49}$Ni$_{21}$Ga$_{30}$ (at.%) alloy with B2-L1$_0$ martensitic transformation and of the disordered iron-based Fe$_{41}$Ni$_{28}$Co$_{17}$Al$_{11.5}$X$_{2.5}$ (X=Ta, Ti) (at.%) alloys, which undergo thermoelastic $\gamma$-\alpha' martensitic transformations, were studied in terms of the influence of chemical composition, size and volume fraction of the dispersed $\gamma'$-phase particles on functional properties – shape memory effect and superelasticity. Single crystals of Co$_{49}$Ni$_{21}$Ga$_{30}$ alloy showed that the precipitation of nanometric $\gamma'$-phase particles changes the martensitic transformation characteristic temperature, reduces the value of the shape memory effect and superelasticity, increases thermal and stress hysteresis, and leads to hardening of the high temperature phase, which promotes superelasticity at a wide temperature range and at high temperatures at T>373K compared with the crystals without particles. Single crystals of FeNiCoAlX (X=Ta, Ti) alloys have experimentally demonstrated that the precipitation of ordered $\gamma'$-phase particles at a size of d=5–10 nm during aging at T=973 K, 3 h, leads to the occurrence of the shape memory effect and superelasticity.

1. Introduction
There is currently a search for new ferromagnetic materials with high strength and functional properties to be used as sensors, detectors, and actuators. One of the most promising ferromagnetic alloys with high strength and good ductility are the ordered CoNiGa alloys with B2-L1$_0$ martensitic transformation (MT) (B2 is the ordered phase based on the volume-centred cubic lattice, L1$_0$ is tetragonal martensite based on the face-centred tetragonal lattice) and the disordered Fe-based alloys with $\gamma$-\alpha' MT ($\gamma$ is a face-centred cubic lattice (fcc), $\alpha'$ is a volume-centred tetragonal lattice (bct)) [1–10]. It is known that, due to the precipitation of dispersed $\gamma'$-phase particles in alloys, not only the strength properties of high-temperature phase, but temperatures of MT, the temperature interval of superelasticity (SE), the type of MT, thermal and stress hysteresis can be controlled [1–10]. In contrast to the ordered CoNiGa alloy in iron-based alloys in a state without particles the MT is non-thermoelastic and shape memory effect (SME) and SE are not observed. Precipitation of dispersed $\gamma'$-phase particles with an atomic ordered L1$_2$-type structure leads to the development of the thermoelastic $\gamma$-\alpha' MT, coherently related to high-temperature phase in iron-based alloys [6, 9–11]. Analysis of the data presented in [4, 6–9, 11] suggests that achieving the conditions for a thermoelastic
γ'-α' MT in iron-based alloys plays an important role not only for the ordered γ'-phase precipitation, but also for its chemical composition, which determines its stability and strength at γ'-α' MT.

Currently there have been no systematic investigations of the influence of chemical composition, size, and volume fraction of dispersed γ'-phase particles on the functional properties of single crystal CoNiGa ordered alloys and on Fe-based disordered alloys. Therefore, in this paper we present the results of studies of the effect of γ'-phase particles on the SME and SE in single crystals of ferromagnetic alloys CoNiGa and FeNiCoAlX (X=Ta, Ti). It is assumed that the regularities of the influence of dispersed particles on the development of MT, SME and SE should be general and should not depend on the specific type (B2-L1_0 or γ'-α') of MT.

2. Materials and discussion of the results

2.1. The shape memory effect and superelasticity in aged [001]-oriented single crystal CoNiGa ordered ferromagnetic alloys at thermoelastic B2-L1_0 martensitic transformation

For studies of SME and SE in the Co_{30}Ni_{30}Ga_{30} (at.%) alloy crystals were selected oriented along the [001] direction, in which under compression, firstly, there is no contribution from the detwinning strain of L1_0-martensite at the value of transformation deformation ε_0, and development of reversible stress-induced MT has a maximum value of transformation strain ε_σ=4.5%. Secondly, the [001]-oriented crystals are characterized by the high level of deforming stresses of B2-phase owing to Schmid factors equalling zero for operating a <100>{110} slip system, in contrast to other orientations of the crystals, in which the Schmid factors of these systems’ slip are high [1-4]. Therefore the crystals were oriented along the [001] direction and had to demonstrate broad temperature interval of stress-induced MT, wide temperature range of SE, maximum values of SME and SE, and narrow thermal and stress hysteresis compared to the other orientations.

SME and SE studies were carried out in two states: single-phase and after aging with nanometric particles. The low-temperature heat treatment at 623 K for 15 minutes was selected for precipitation of nanometric γ'-phase particles. Electron microscopy found that after aging at T=623 K, 15 minutes, γ'-phase particles form a spherical shape 5 nm in size and a volume fraction f=10^-12%. Figure 1 shows the results of studies of critical stresses σ_σ for stress-induced L1_0-martensite within a broad temperature range of T=100K÷573K for the [001]-oriented single-phase crystals and crystals with γ'-phase particles. It can be seen that in the single-phase state, σ_σ(T) is experiencing one linear stage in which σ_σ increases with increasing test temperature with a=σ_σ/dT=1.88 MPa/K. Such dependence on the σ_σ(T) stage is associated with the development of stress-induced MT, which is described by the Clausius–Clapeyron relation [12]:

\[ \frac{dσ_σ}{dT} = \frac{ΔH}{ε_σT_0} \]

(1)

where ΔH and ΔS are the enthalpy and entropy changes, respectively, ε_σ is transformation strain for B2-L1_0 MT, which depends on crystal orientation, and T_0 is the chemical phase-equilibrium temperature. It can be seen that precipitation of the particles leads to the emergence of stages on σ_σ(T) with α_1=1.10 MPa/K in the interval σ_σ=10÷200 MPa and α_2=1.58 MPa/K at σ_σ=200÷700 MPa (Figure 1), to a decrease in martensitic start (M_s) transformation temperature on 173 K (±2 K) and to a decrease in the value of α compared to the single-phase state. For an explanation of stages on σ_σ(T) and changes in the value of α in the aged crystals, SME was studied under stress.

Study of SME at cooling/heating at different levels of externally applied stresses σ_σ from 10 MPa to 300 MPa showed that for both single-phase (Figure 2a) and aged crystals (Figure 2b), SME was realized at minimum stresses of σ_σ=10 MPa. Consequently, these stresses are sufficient to destroy the self-accommodation structure of L1_0-martensite, and the growth of oriented L1_0-martensite occurs at the development of MT under σ_σ=10 MPa. In this case, the value of SME in single-phase crystals ε_{SME}=4.1% and this value is close to the theoretically calculated value of the lattice deformation ε_σ for the [001]-oriented crystal at B2-L1_0 MT. In crystals with nanometric γ'-phase particles the value of ε_{SME}=2% and it is less in 1.5–2 times as compared with the single-phase state. An estimate of the SME
by the relation [2]: \( \varepsilon_{\text{SME}} = \varepsilon_0 (1-f) \) shows that the value of \( \varepsilon_{\text{SME}} \) should be equal to 3.96% and this value is greater than that experimentally observed. Therefore, the decrease in the value of \( \varepsilon_{\text{SME}} \) at aging is associated not only with a decrease in the volume of material undergoing MT by particles’ precipitation as the particles themselves are not experiencing MT, but also to the influence of the particles on the nucleation and growth of martensite under \( \sigma_{\text{ext}} \) [5]. This trend was observed earlier in [123] Co49Ni21Ga30 single crystals [1, 2].

**Figure 1.** Temperature dependence of critical stresses \( \sigma_{\text{cr}} \) for [001]-oriented single crystals Co49Ni21Ga30 alloy in compression: 1 – single-phase crystals and 2 – crystals with particles.

**Figure 2.** The curves of the dependence of the shape memory effect \( \varepsilon_{\text{SME}} \) at the level of applied external stress \( \sigma_{\text{ext}} \) for [001]-oriented single crystal Co49Ni21Ga30 (at.%) alloy at compression deformation: a – single-phase crystals and b – crystals with particles.

In [1, 2] it is shown that the stresses \( \sigma_{\text{cr}} \) depend not only on the transformation strain, but also on the energy dissipation which is characterized by the thermal hysteresis \( \Delta T^\sigma = A\sigma^\sigma - M_s^\sigma \). Figure 2 shows that in single-phase crystals the value of SME \( \varepsilon_{\text{SME}} \) and the thermal hysteresis \( \Delta T^\sigma = 22\text{K} \) with increasing \( \sigma_{\text{ext}} \) do not change, and curve \( \sigma_{\text{cr}}(T) \) has one stage. In the aged crystals with increasing \( \sigma_{\text{ext}} \) the value of \( \Delta T^\sigma \) decreases, ranging \( \sigma_{\text{cr}} = 10-200\text{ MPa} \), and a sharp decrease is seen in the \( \Delta T^\sigma \), while \( \sigma_{\text{cr}} > 200\text{MPa} \) the value of \( \Delta T^\sigma \) varies only slightly. This may be one of the causes of the two stages on \( \sigma_{\text{cr}}(T) \) depending on different values of \( \alpha \) in the aged [001]-oriented crystals of the B2-L1\(_0\) MT [2].

It is shown that the precipitation of \( \gamma' \)-phase particles leads to expansion of the temperature range of SE on 80K compared to the single-phase crystals, \( \Delta T_{SE} = 370\text{K} \), and for the latter a perfect loop SE was observed at \( T \geq 573 \text{ K} \). This is due to the influence on particles of the stress level of the high-temperature phase and \( M_s \) temperature. Figure 3 shows the curves for single-phase and aged crystals.
A comparison of SE curves shows that the precipitation of particles leads to a decrease in the value of SE $\varepsilon_{\text{SE}}$ 1.5 times, to increase the magnitude of stress hysteresis $\Delta\sigma$ 3.8 times, and the development of MT under $\sigma>\sigma_{\text{cr}}$ with a high strain hardening coefficient $\theta=d\sigma/d\varepsilon$ compared with the single-phase state.

Figure 3. Superelasticity curves of [001]-oriented single crystals Co$_{49}$Ni$_{21}$Ga$_{30}$ (at.%) alloy at $T=298$K in: a) single phase and b) aged crystals.

2.2. Shape memory effect and superelasticity in aged [001]-oriented single crystals of ferromagnetic disordered iron-based alloys

For the study of SME and SE in disordered iron-based alloys Fe$_{41}$Ni$_{28}$Co$_{17}$Al$_{11.5}$X$_{2.5}$ (X=Ta, Ti) (at. %) at tensile deformation crystals were selected that were oriented along the [001] direction in which, during tensile deformation, the value of the lattice strain $\varepsilon_0=8.7$ % for $\gamma$-Fe MT has a maximum value. This would provide a maximum resource of reversible deformation in the study of SME and SE [7]. For the precipitate of the ordered $\gamma'$-phase aging at $T=973$ K, 3 h was chosen, to clarify the effect of particles of similar size, $d=5–10$ nm, and different chemical compositions, as a result of variation of the fifth element, while maintaining the atomic concentration of the alloy on the nature of stress-induced MT and values of SME and SE.

Figure 4 shows the temperature dependence of the critical stresses $\sigma_{\text{cr}}$ at tension for [001]-oriented single crystals of Fe$_{41}$Ni$_{28}$Co$_{17}$Al$_{11.5}$X$_{2.5}$ (X=Ta, Ti) alloys at a wide temperature range of 77–550 K. It can be seen that on depending of $\sigma_{\text{cr}}(T)$ two stages are observed that are characteristic for alloys undergoing stress-induced MT. At the first stage 77 K <$T<M_d$ ($M_d$ is the temperature at which the critical stress level of the high-temperature phase is equal to the critical stress level for martensite under stress), $\sigma_{\text{cr}}$ increases with increasing test temperature: it is close to a linear dependence and is described by the relation Clausius-Clapeyron (1). At $T>M_d$ is the second stage, which is connected with the deformation of the high-temperature phase and is characterized by a normal temperature dependence of the critical stress of typical FCC materials [13].

Figure 4 shows that the variation of the chemical composition of the $\gamma'$-phase particles leads to a change in the $M_d$ temperature, in stress in temperature $T=M_d$, and therefore in the temperature range of stress-induced MT $\Delta T_{\text{SIM}}$ (first stage). The stress at $T=M_d$ in [001] single crystals of FeNiCoAlTa alloy equal 1043 MPa, and FeNiCoAlTi alloy $\sigma_{\text{cr}}(M_d)$=900 MPa. The temperature at point $M_d$ in crystals of FeNiCoAlTa also has a maximum value and is equal to 423 K, that less on 117 K is compared to in crystals FeNiCoAlTi alloy, where $T(M_d)$=306 K. Such a difference in the temperature and stresses at the point of $M_d$ leads to a different temperature range of stress-induced MT $\Delta T_{\text{SIM}}$: in crystals of FeNiCoAlTa $\Delta T_{\text{SIM}}=346$ K, and in crystals of FeNiCoAlTi, $\Delta T_{\text{SIM}}=229$ K. The value of $\alpha=d\sigma_{\text{cr}}/dT$ after aging at 973 K for 3 h also depends on the chemical composition of the $\gamma'$-phase particles and equals 3.3 MPa/K in crystals of FeNiCoAlTa, and in crystals of FeNiCoAlTi $\alpha=d\sigma_{\text{cr}}/dT=4.8$ MPa/K.

It has been experimentally established that the precipitation of $\gamma'$-phase particles at $T=973$ K for 3 h in [001]-oriented crystals of FeNiCoAlX (X=Ta, Ti) alloys leads to the manifestation of SME and SE. The value of SME $\varepsilon_{\text{SME}}$ and SE $\varepsilon_{\text{SE}}$, temperature range of SE $\Delta T_{\text{SE}}$ and value of thermal $\Delta T^\sigma$ and stress $\Delta\sigma$ hysteresis depends on the chemical composition of the alloy (Figs. 4, 5, 6).
Figure 4. Temperature dependence of the critical stresses $\sigma_{cr}$ for [001]-oriented crystals aged at $T=973$ K for 3 h at tensile deformation: curve 1 – FeNiCoAlTa alloy, 2 – FeNiCoAlTi.

Figure 5 shows the results of the research of the value of SME in the experiment during cooling/heating under constant tensile stress. From the figure it can be seen that in [001]-oriented single crystals of FeNiCoAlX (X=Ta, Ti) alloys during aging at $T=973$ K for 3 h at a constant external stress the reversible one-stage $\gamma$-$\alpha'$ MT is implemented. The value of thermal hysteresis $\Delta T$ under maximum applied stress defined on middle-loop stress hysteresis in FeNiCoAlTa alloys is equal to 50 K. This value $\Delta T$ at more than 1.8 times in the FeNiCoAlTi alloy (Figure 5). The maximum value of the SME in FeNiCoAlTa crystals is equal $\varepsilon_{SME}=4.2\%$, and in FeNiCoAlTi crystals $\varepsilon_{SME}=3\%$. In such a relationship the values correlated with equation (1), at that the ratio of the value $\alpha(Ti)/\alpha(Ta)=1.4$ coincides with the value $\varepsilon_{SME}(Ti)/\varepsilon_{SME}(Ta)=1.4$. The experimentally observed value of SME $\varepsilon_{SME}$ in [001]-oriented crystals FeNiCoAlX (X=Ta, Ti) alloys is less than the theoretically calculated values of the lattice strain for the $[001]$ $\varepsilon_0=8.7\%$ at the $\gamma$-$\alpha'$ MT [6]. The reason for the decrease in the value of SME is to reduce the volume of material undergoing MT, the presence in the alloys of TaC, TiC particles, which are formed in the melting process of the alloy, and single crystal growth.

The temperature range of SE in [001]-oriented single crystals of FeNiCoAlTi and FeNiCoAlTa alloys is close and equals $\Delta T_{SE}=129$ K (Figure 4). A maximum value of SE $\varepsilon_{SE}$, defined in experiments on cycling, equals 4.1% (Figure 6) and, as with the value of SME $\varepsilon_{SME}$ is less than the theoretical value $\varepsilon_0$ [6]. The value of stress hysteresis $\Delta \sigma$ at a one-test temperature $T=77$ K depends on the composition of the alloy (Figure 6). In [001]-oriented single crystals FeNiCoAlTa alloy $\Delta \sigma=52$ MPa and in [001]-oriented single crystals FeNiCoAlTi alloy $\Delta \sigma=75$ MPa. Changing stress hysteresis $\Delta \sigma$ in alloys is associated with the different critical stress levels in the high-temperature phase in these alloys.
Figure 6. Stress-strain (σ-ε) curves of superelasticity in the [001]-oriented single crystals aged at T=973 K for 3 h at tensile deformation. Test temperature T=77 K: a - FeNiCoAlTa alloy, b - FeNiCoAlTi

3. Conclusion

These studies on the single crystals of ferromagnetic Co_{49}Ni_{31}Ga_{30} and Fe_{41}Ni_{28}Co_{17}Al_{11.5}X_{2.5} (X=Ta, Ti) alloys show that precipitation of nanometric particles of different chemical composition, size, and volume fraction is a promising approach towards the creation of a new class of high-strength materials with SME and SE. Dispersed particles do not experience MT, but enable by variations in their chemical composition, size and volume fraction control of both the mechanical and functional properties and thus facilitate acquisition of materials with the required performance properties. Precipitation of the particles in the ordered Co_{49}Ni_{31}Ga_{30} alloy leads to the manifestation of SE not only with a wide interval, but also at high temperatures up to 573 K, and the precipitation of ordered γ'-phase particles in size d=5÷10 nm in disordered Fe_{41}Ni_{28}Co_{17}Al_{11.5}X_{2.5} (X=Ta, Ti) alloys contributes towards a change in the kinetics of MT from non-thermoelastic to thermoelastic and observation SME and SE.

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References
[1] Kireeva I V, Pons J, Picornell C, Chumlyakov Yu I, Cesari E and Kretinina I V 2013 Intermetallics 35 60–66
[2] Kireeva I V, Picornell C, Pons J, Kretinina I V, Chumlyakov Yu I and Cesari E 2014 Acta Mat 68 127–139
[3] Dadda J, Maier H J, Niklasch D, Karaman I, Karaca H E and Chumlyakov Y I 2008 J. Physical Metall and Mat Science 39 2026–2039
[4] Chumlyakov Y I, Kireeva I V, Panchenko E Y, Timofeeva E E, Pobedennaya Z V, et al. 2008 Russ Phys J 51 1016
[5] Chumlyakov Yu, Kireeva I and Panchenko E 2011 Russ Phys J 54 96–108
[6] Chumlyakov Yu, Kireeva I, Panchenko E, Karaman I, Maier H J and Timofeeva E 2013 J of Alloys and Compounds 577 S393–S398
[7] Tanaka Y, Himuro Y, Kainuma R, et al. 2010 J Science 327 1488–1490
[8] Chumlyakov Yu I, Kireeva I V, Panchenko E Y, Zakharova E G, Kirillov VA, Efimenko S P and Sehitoglu H 2004 Doklady Physics 49 47–50
[9] Omori T, Abe S, Tanaka Y, Lee G Y, Ishida K and Kainuma R 2013 J. Scripta Mat 69 812–815
[10] Chumlyakov Yu I, Kireeva I V, Kretinina I V, Keynih K S, Kuts O A, Kirillov V A, Karaman I and Maier H 2013 Russ Phys J 56 66–74
[11] Kokorin V V and Gun'ko L P 1995 Metal Physics and Advanced Technologies 17 30–35
[12] Otsuka K and Wayman C M 1998 Shape memory materials Cambridge University Press 284
[13] Chumlyakov Yu I, Kireeva I V, Korotaev A D, Litvinova E I, Zuev Y L 1996 Russ Phys J 3 189–210