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The cyclic stability of rubber-like behaviour in stress-induced martensite aged Ni₄₉Fe₁₈Ga₂₇Co₆ (at.%) single crystals

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ABSTRACT

In present work, the cyclic stability of the rubber-like behaviour (RLB) was investigated in $Ni_{49}Fe_{18}Ga_{27}Co_{6}$ (at. %) single crystals. Crystals were aged in the martensite phase at 423 K for 1 h under a compressive stress of 450 MPa, applied along the $[1\,1\,0]_{B2}||[1\,0\,0]_{L10}$ -direction. The RLB was induced by a preliminary chemical stabilization of the oriented $L1_{0}$ -martensite during stress-induced martensite aging (SIM-aging) and following the reversible reorientation of martensitic variants under a compressive stress applied along the $[0\,0\,1]_{B2}||[0\,0\,1]_{L10}$ -direction. The high cyclic stability of the RLB was obtained in 200 loading/unloading cycles, due to the low reorientation stresses of the $L1_{0}$ -martensite variants (no higher than 140 MPa) and the high strength properties of the $L1_{0}$ -martensite (\sim 1.6 GPa). The irreversible strain after 200 cycles did not exceed 0.6%. An increase in the number of cycles did not lead to the effect of destabilization of the $L1_{0}$ -martensite.

1. Introduction

The single crystals of a ferromagnetic NiFeGaCo shape memory alloy are of great practical interest as sensors and actuators, due to their unique functional properties. These materials exhibited high-temperature superelasticity (SE), up to 673 K, a large reversible strain (up to -6.3% in compression and up to +12.5% in tension) [1], a magnetic field-induced strain [2] and an elastocaloric effect [3]. Recent studies on NiFeGaCo single crystals [4,5] have shown that a two-way shape memory effect (TWSME), up to +9.0%, can be induced by SIMaging. Diffusion is involved in the process and is related to the reconfiguration of atoms and point defects, in compliance with a martensite symmetry and twin structure [6,7]. This causes a chemical stabilization of the stress-induced martensite and growth of the latter upon subsequent stress-free cooling, inducing TWSME.

The stabilized variant of thermal-induced martensite can be reoriented under applied stress into another variant of stress-induced martensite. This process is accompanied by reversible strain and is known as rubber-like behaviour (RLB) [6,7]. In works [4,5,8] on SIMaged NiFeGaCo and NiMnGa single crystals, the RLB, with a reversible strain of $-13 \div -16\%$ under compressive stresses, no more than 150 MPa, was obtained. This may be of great practical importance.

Previously, RLB induced by the aging in martensite was obtained on Cuand Au-based alloys [9,10]. But due to very low cyclic and thermal stability of this effect, no further studies were carried out and RLB did not find wide application. It is assumed that the regime of SIM-aging for ferromagnetic NiFeGaCo alloy, introduced in our previous works [4,5], provides a multiple reproduction and high cyclic stability of the RLB. Therefore, the aim of this work was to investigate the cyclic stability and degradation mechanisms of the RLB during loading/unloading tests in SIM-aged Ni₄₉Fe₁₈Ga₂₇Co₆ (at.%) single crystals.

2. Materials and methods

Single crystals of the $Ni_{49}Fe_{18}Ga_{27}Co_6$ (at.%) alloy were grown by the Bridgman technique. The crystals were preliminarily annealed at 1448 K for 1 h, followed by water quenching. The initial phase had a B2-lattice. Samples for research had facets with crystallographic indexes, as shown in Fig. 1, a. The most effective regime of SIM-aging was selected from Refs. [4,5]: aging at 423 K for 1 h under compressive stress of 450 MPa applied along the $[1\,1\,0]_{B2}$ -direction. This regime was chosen to avoid a plastic flow and to obtain a stabilized martensite variant, which subsequently gave the tensile TWSME along the perpendicular $[0\,0\,1]_{B2}$ -direction (Fig. 1, a). The SIM-aging and the investigations of RLB were

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E.E. Timofeeva et al. Materials Letters 300 (2021) 130207

carried out on an electromechanical testing machine, Instron 5969. The TWSME was studied on the dilatometer under stress-free conditions ($\sigma \rightarrow 0$ MPa). Electron microscopic studies were performed using the transmission electron microscope (TEM), HT-7700 Hitachi, at the "Krasnoyarsk Science Center SB RAS".

3. Results and discussion

The SIM-aging along the $[1\,1\,0]_{B2}$ -direction led to the chemical stabilization of the L10-martensite variant, and the appearance of tensile TWSME along the perpendicular $[0\,0\,1]_{B2}$ -direction (Fig. 1, b). The TWSME strain was + 8.3(±0.3)%. The TWSME testifies about the efficiency of SIM-aging and degradation mechanisms during cyclic tests of RLB, which include a destabilization of martensite. So, the detailed consideration of TWSME of SIM-aged single crystals is required to be studied before and after the RLB cycling.

According to the crystallographic calculations of transformation strain during $B2\text{-L}1_0$ MT [4], the formation of the martensite variant V1 leads to a tension along the $[001]_{B2}$ -direction (Table 1). Hence variant V1 is appeared during TWSME. The theoretical strain along the $[001]_{B2}$ -direction is +6.3% at the formation of the twinned L10-martensite and is +14.5% in the case of complete detwinning [4]. The decrease in the experimental strain $+8.3(\pm0.3)\%$ in comparison with the theoretical resource, +14.5%, is associated with the formation of other L10-martensite variants V2/V3 with a compressive strain of -6.3% along the $[001]_{B2}$ -direction. Martensite variants of V2/V3 arose, due to an incomplete detwinning of martensite during SIM-aging and internal stress fields on plastically deformed regions. Two L10-martensite variants (main variant V1 and additional V2/V3) and single dislocations were observed by TEM at 300 K (Fig. 2, a).

Next, a compressive stress was applied along the $[0\,0\,1]_{B2}\text{-direction}$ at 300 K below the temperature M^{*}_{f} to obtain the RLB as shown on Fig. 1, a. Fig. 3, a shows the $\sigma(\epsilon)$ curves during isothermal loading/unloading cycles from 1 to 200.

The reorientation from the stabilized martensite variant V1 to a favourable stress-induced variant (V2 or V3) occurred at the RLB. This process was accompanied by the reversible strain $\epsilon_{rev}=-14.5(\pm0.3)\%$. The theoretical transformation strain at B2-L1 $_0$ MT ($\epsilon_{CVP+detwin}=-6.3\%$) are not appropriate for analysis of the RLB strain, because MT does not occur in this case. Detailed crystallographic calculations, describing the martensitic variants' reorientation, are presented in [5]. The theoretical reorientation strain from variant V1 to V2/V3 under compression along the $[001]_{B2}||[001]_{L10}\text{-direction}$ is -16.6% [5]. Consequently, the theoretical strain resource was not realized during the RLB. This is associated with incomplete detwinning of the L1 $_0$ -martensite during SIM-aging and the presence of martensite variants V2/V3 in the initial structure.

Table 1
Lattice correspondence variants and theoretical transformation strain for the NiFeGaCo alloy [4].

Variant	Orientation corresponds to $[110]_{B2}$	Theoretical strain for the B2-L1 $_{0}$ MT along the [001] $_{\mathrm{B2}}$ -direction	
		ϵ_{CVP} ,%	$\epsilon_{\text{CVP+detwin}}$ %
V1	[100] _{L10}	+6.3	+14.5
V2	$[\overline{1}12]_{10}$	-3.0	-6.3
V3	$[\overline{1}12]_{L10}$	-3.0	-6.3

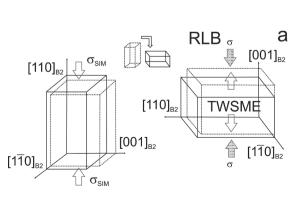
The interaction of different martensite variants leads to an increase in elastic and dissipated energies. As a result, the stress hysteresis and reorientation stresses increase with a strain degree. The stored elastic energy contributes to the reverse reorientation of the martensite variants, which occurs at the constant stress level, σ_r , during unloading. Therefore, the strain hardening coefficient at unloading $\theta_u = d\sigma/d\epsilon = 0.5 \cdot 10^2 \text{MPa}$ is 5 times less than $\theta_1 = 2.6 \cdot 10^2 \text{MPa}$ at loading.

The following RLB parameters were calculated to analyse the $\sigma(\epsilon)$ curves, depending on the cycle number: reversible ϵ_{rev} and irreversible ϵ_{irr} strains, critical stress of the start of reorientation, σ_{cr} , stress at the centre of the loading plateau, σ_m , stress of the reverse reorientation, σ_r and stress hysteresis, $\Delta\sigma$ (Fig. 3, b).

The dependences of the parameters on the cycle number can be divided into three stages. A noticeable degradation only occurs at the first stage (1–3 cycles). The stresses, σ_{cr} and σ_m and hysteresis, $\Delta\sigma$, decrease by 16–20%. This feature is typical for other functional properties of shape memory alloys – TWSME and SE [11,12]. The second stage is observed in 4–90 cycles, in which σ_m and $\Delta\sigma$ do not change, and there is a slight decrease in σ_{cr} by 6 MPa (less than 1% for every 3 cycles). Furthermore, the stage of stable RLB is observed during 90–200 cycles, when the $\sigma(\epsilon)$ curves do not change.

The stress of the reverse reorientation at unloading, σ_r , does not depend on the cycle number and remains practically constant during cycling. The stress at the centre of the loading plateau, σ_m , only changes in the first 3 cycles, and the $\theta_l=d\sigma/d\epsilon$ at loading does not change at all. Consequently, the cycling has practically no effect on the main process of forward and reverse reorientation of the martensite variants.

The reversible strain decreases slightly to $-13.9(\pm0.3)\%$ with an increase in cycle number from 1 to 200, due to the appearance of irreversible strain $\epsilon_{irr}=0.6\%$. The reason for the accumulation ϵ_{irr} is the formation of dislocations. The stress fields from dislocations facilitate the appearance of the favourable stress-induced martensite variant V2/V3 and reduce the critical stress σ_{cr} (Fig. 3, b). Indeed, an increase in the dislocation density after 200 cycles was observed by TEM (Fig. 2, b). At the same time, the TWSME strain did not change after 100 and 200 RLB cycles (Fig. 1, b). Consequently, destabilization of the martensite variant



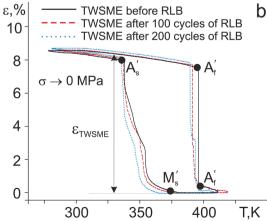


Fig. 1. The schemes of SIM-aging TWSME and RLB (a), ε(T) curves of tensile TWSME along the [001]_{B2}-direction, obtained before RLB and after RLB cycling (b).

E.E. Timofeeva et al. Materials Letters 300 (2021) 130207

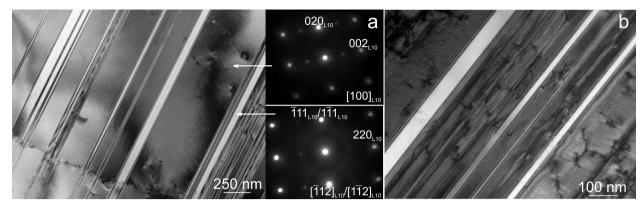
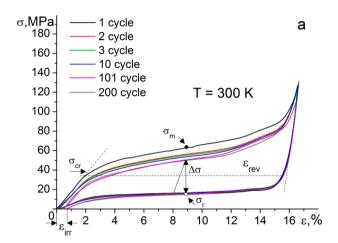


Fig. 2. Microstructure of SIM-aged single crystals: before the RLB, zone axis are $[110]_{B2} || [100]_{L10}$ (variant V1) $|| [\overline{1}12]_{L10}$ (variant V2) or $[\overline{1}12]_{L10}$ (variant V3) (a); after 200 RLB cycles (b).



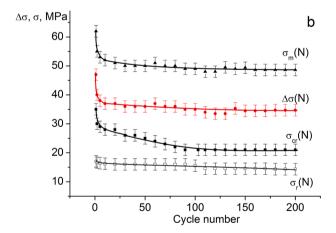


Fig. 3. The $\sigma(\epsilon)$ curves during the RLB under compression along $[001]_{B2}$ -direction (a), the dependences of the RLB characteristic parameters on the cycle number (b).

V1 did not occur during the RLB cycling.

The reasons for the high cyclic stability of RLB are, firstly, the low stresses of reorientation (no more, than 140 MPa) and the high yield strength level of L10-martensite ($\sim \! 1.6$ GPa). This ensures the suppression of elastic energy relaxation upon reorientation. Secondly, the low temperature of the RLB, much lower than the SIM-aging temperature, contributes to the low rate of diffusion and does not cause destabilization of oriented L10-martensite, which takes place during high-temperature tests [5].

4. Conclusion

The cyclic stability of RLB was investigated on $Ni_{49}Fe_{18}Ga_{27}Co_6(at.\%)$ single crystals. The RLB with the strain of $\epsilon_{rev}=-14.5(\pm0.3)\%$ was obtained at 300 K under compression along the $[0\,0\,1]_{B2}$ -direction in the SIM-aged single crystal. A high cyclic stability of the RLB was observed during 200 loading/unloading cycles. The reversible strain decreased slightly to $-13.9(\pm0.3)\%$ during the 200 cycles, due to the accumulation of the irreversible strain of 0.6%. The change in the RLB characteristics (level of reorientation stress and stress hysteresis) up to 16-20% of the value occurred in the first 3 cycles. A slight decrease in the critical stress of the martensite variants' reorientation was observed during 4-90 cycles. The RLB remained stable during 90-200 cycles.

The reasons for the high cyclic stability of RLB are the high strength properties of martensite and the low temperatures and stresses for reorientation. Such a combination only led to the formation of single dislocations. The stress fields from dislocations reduced the critical stresses of the twin boundaries motion. The cycle number had practically no effect on the main process of direct and reverse reorientation of martensite variants, and did not lead to the destabilization of the L1 $_{\rm 0}$ -martensite.

CRediT authorship contribution statement

E.E. Timofeeva: Conceptualization, Resources, Writing - original draft, Project administration. **E.Yu. Panchenko:** Conceptualization, Writing - original draft, Writing - review & editing. **A.B. Tokhmetova:** Investigation, Visualization. **A.S. Eftifeeva:** Investigation. **Yu.I. Chumlyakov:** Conceptualization, Writing - review & editing, Supervision. **M.N. Volochaev:** Investigation, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] E. Panchenko, Y. Chumlyakov, H.J. Maier, et al., Intermetallics. 18 (2010) 2458–2463.
- [2] H. Morito, A. Fujita, K. Oikawa, et al., Appl. Phys. Lett. 90 (2007), 062505.
- [3] F. Xiao, M. Jin, J. Liu, et al., Acta Mater. 96 (2015) 292–300.
- [4] E. Panchenko, A. Tokhmetova, N. Surikov, et al., Scr. Mater. 194 (2021).

E.E. Timofeeva et al. Materials Letters 300 (2021) 130207

- [5] E. Panchenko, E. Timofeeva, A. Eftifeeva, et al., Scr. Mater. 162 (2019) 387-390.

- [6] K. Otsuka, X. Ren, Mater. Sci. Eng. A 312 (2001) 207–218.
 [7] P. Kadletz, P. Krooß, Yu. Chumlyakov, et al., Mater. Lett. 159 (2015) 16–19.
 [8] E. Panchenko, E. Timofeeva, M. Pichkaleva, et al., Shap. Mem. Superelasticity 6 (2020) 29–34.

- [9] Y. Murakami, Y. Nakajima, K. Otsuka, et al., Mater. Sci. Eng. 237 (1997) 87–101.
 [10] D. Xue, Y. Zhou, X. Ding, et al., Phys. Rev. B 86 (2012).
 [11] C. Yu, G. Kang, Q. Kan, J. Mech. and Phys. of Solids 82 (2015) 97–136.
 [12] K. Atli, I. Karaman, R. Noebe, et al., Mater. Sci. Eng. A 560 (2013) 653–666.