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Martensite aging in ⟨001⟩ oriented $Co_{49}Ni_{21}Ga_{30}$ single crystals in tension

C. Lauhoff[*,§], P. Krooß[*], D. Langenkämper[†], C. Somsen[†], G. Eggeler[†], I. Kireeva[‡],
Y. I. Chumlyakov[‡] and T. Niendorf[*]

[*]*Institut für Werkstofftechnik (Materials Engineering)*
Universität Kassel, 34125 Kassel, Germany

[†]*Institut für Werkstoffe, Ruhr-Universität Bochum*
44801 Bochum, Germany

[‡]*Siberian Physical Technical Institute, Tomsk State University*
Novosobornay Square 1, 634050 Tomsk, Russia
[§]*lauhoff@uni-kassel.de*

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Co–Ni–Ga high-temperature shape memory alloys (HT-SMAs) are well-known candidate materials for damping applications at elevated temperatures. Recent studies showed that upon heat treatment in stress-induced martensite under compressive loads transformation temperatures can be increased significantly, qualifying Co–Ni–Ga for HT-actuation. The increase in transformation temperatures is related to a change in chemical order recently validated via neutron diffraction experiments. Since SMAs show distinct tension–compression asymmetry in terms of theoretical transformation strains and bearable stresses, understanding the impact of martensite aging in tension is crucial for future applications. The current results indicate that martensite aging in tension provides for a further improvement in functional properties.

Keywords: High-temperature shape memory alloys, actuation, SIM aging, Co–Ni–Ga, martensite stabilization.

Shape memory alloys (SMAs) have received considerable attention over the last decades.[1–5] Their unique functional properties are based on a thermo-elastic, fully reversible phase transformation from a high-temperature austenitic phase to a low-temperature martensitic phase, being characterized by a high and low degree of symmetry, respectively.[1,4,5] As is known from literature, the thermo-elastic nature of martensitic transformation strongly affects phase transition,[1] such that findings available for martensitic phase transformation in non-thermo-elastic alloys, e.g. in Ref. 6, cannot be directly transferred to SMAs, e.g. Co–Ni–Ga being in focus of the current study. Due to the large reversible strains, SMAs are attractive for applications as solid state actuators or damping devices in various fields.[2,3,7] Particularly in the aerospace and automotive sectors application temperatures often exceed 100°C. However, conventional Ni–Ti SMAs are limited to application temperatures of about 80°C hindering their technological breakthrough in these fields.[1,2,4,5] In order to widen the application range in terms of higher operating temperatures and higher reversible strains, several new alloy systems, featuring increased martensite start temperatures (M_s), were introduced in recent years and referred to as high-temperature (HT-) SMAs.[4,8] Ternary Ni–Ti–X (X = Pt, Pd, Hf, Zr), Cu-based, Ti–Ta-based and Ni–Mn–X alloys have been proposed as attractive candidates for HT-SMA applications.[3,4,9–11] However, most HT-SMAs consist of expensive alloying elements and/or are brittle. Most importantly they show a poor cyclic stability, caused by distinct microstructural instabilities.[4,9,12] In this regard, the Heusler-type Co–Ni–Ga alloy represents an attractive alternative: it consists of relatively inexpensive alloying elements and shows an improved workability due to the potential precipitation of a ductile second phase.[11,13,14] Due to a fully reversible pseudoelastic response at temperatures up to 500°C, Co–Ni–Ga HT-SMAs are promising candidates for high-temperature damping applications.[15,16]

A recently introduced design concept aims at significantly increasing the transformation temperatures based on aging of

[§]Corresponding author.

stress-induced martensite, referred to as stress-induced martensite aging (SIM-aging).[17] The SIM-aging treatment stabilizes the martensite and leads to an increase of the M_s temperature by about 130°C in the Co–Ni–Ga system.[17] By means of neutron diffraction, the underlying microstructural mechanism responsible for this martensite stabilization has been identified as change of chemical order in the martensitic phase.[18] Ren and Otsuka linked this diffusive re-ordering mechanism to the concept of symmetry-conforming short-range order (SC-SRO) in 1997.[19] The martensite stabilization is related to a decrease of the free energy resulting from symmetry conform atomic re-arrangements of lattice imperfections within sub-lattices.[19,20] Stabilization of both, the martensitic and austenitic phase, through a change in chemical order has been recently shown by Bruno *et al.*[21] in the Heusler-type Ni–Co–Mn–In meta-magnetic SMA.

In addition to re-ordering phenomena, a variety of further microstructural mechanisms contributing to martensite stabilization have been identified in the last decades.[19,20,22–24] One important mechanism is based on detwinning of martensite, leading to the necessity of forming new habit planes between austenite and the detwinned martensite.[23] Another effect appears to be related to an immobilization of moving interfaces by point defects.[22] Martensite stabilization has been regarded as detrimental in the past, as in many SMAs the corresponding shift of transformation temperatures proceeds in an uncontrollable manner, hindering robust actuator applications.[22–27] In contrast, the SIM-aged Co–Ni–Ga has been shown to be cyclically stable at elevated temperatures.[17]

The Co–Ni–Ga system features a pronounced transformation asymmetry with respect to the applied stress state.[28] Maximum transformation strains of -4.8 and 8.6% in compression and tension, respectively, were found experimentally and rationalized using energy minimization theory for the $\langle 001 \rangle$-crystal orientation.[28–30] In applications, Co–Ni–Ga HT-SMAs will be subjected to both, compressive and tensile loading. In a previous study,[17] the SIM-aging procedure was characterized under compressive loads. The current study addresses the response of a SIM-aged material to tensile loading and focuses on the cyclic functional stability during load biased thermal cycling.

Large $\langle 001 \rangle$-oriented single crystals of $Co_{49}Ni_{21}Ga_{30}$ were grown in a helium atmosphere using the Bridgeman technique. Dog-bone-shaped samples with a gauge length of 18 mm and a cross-section of 1.5*1.5 mm^2 were machined from bulk single crystals by electro discharge machining (EDM) such that the load axes were parallel to the $\langle 001 \rangle$ direction of the austenitic phase. In order to remove the EDM affected surface layer, the samples were mechanically ground. For solution heat treatment, the samples were encapsulated in quartz glass tubes under argon atmosphere and then solutionized for 12 h at 1200°C followed by air cooling.

Mechanical tests were carried out on a servohydraulic test rig. Strain measurement was realized by employing a high-temperature extensometer with a gauge length of 12 mm and ceramic extension rods, directly attached to the specimen. Heating–cooling experiments were conducted using controlled convection furnaces. Temperatures were measured on the sample surface using a pyrometer with a measuring spot of 0.6 mm. The SIM-aging procedure under superimposed tensile load was conducted for 20 min at 400°C in 100% martensite. Samples were air cooled and finally unloaded. Further experimental details of the SIM-aging procedure are given in Ref. 17. Following SIM-aging, thermomechanical heating–cooling experiments were performed using heating/cooling rates of 2.5°C s^{-1}. Superimposed constant tensile stresses ranging from 50 to 125 MPa were applied. In order to evaluate the cyclic stability of the strain-temperature behavior, the specimens were subjected to 30 thermal cycles. Microstructural analysis was conducted using a transmission electron microscope (TEM) operating at a nominal voltage of 200 kV. The TEM samples were extracted perpendicular to the loading direction from the crystals using focused ion beam TEM foil micromachining in a FEI Quanta 200 3D.

For the solutionized condition, differential scanning calorimetry (DSC) measurements (not shown for the sake of brevity) revealed that the austenite start (A_s) and martensite start (M_s) temperatures are 32.7 and 9.2°C, respectively. Consequently, following cooling from the high temperature regime, the austenitic phase is stable at room temperature. Figure 1 shows TEM micrographs of Co–Ni–Ga after SIM-aging for 20 min at 400°C under tensile load. As is apparent from Fig. 1(b), a single phase twinned martensite microstructure is identified by selected area electron diffraction (SAED). Thus, the aging treatment of the stress-induced martensite led to the stabilization of the martensitic phase which is attributed to changes in chemical order.[17–20]

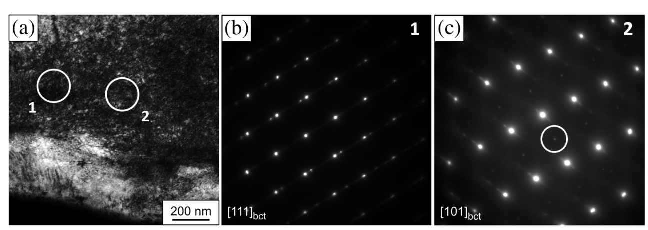
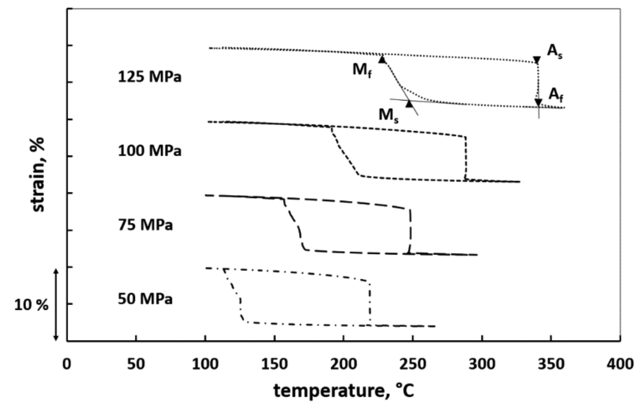
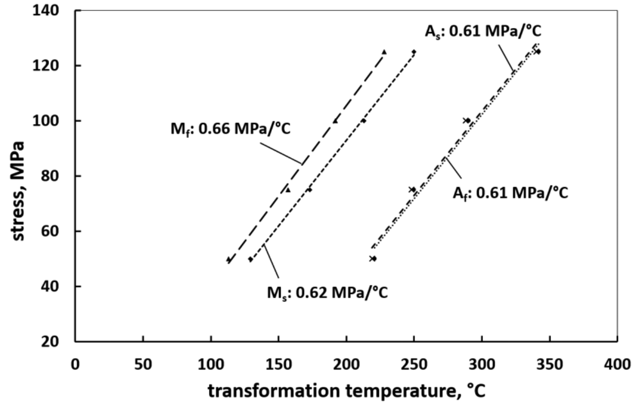


Fig. 1. TEM analysis of the microstructure of Co–Ni–Ga following SIM-aging for 20 min at 400°C under tensile load. Bright field image (a) in [101] zone direction with local areas indicated by the white circles, where the corresponding SAED pattern (b and c, b obtained after tilting) were recorded. The results show twinned martensite (b) and a weak degree of order, i.e. weak superlattice reflections (encircled in white in c) after SIM-aging.



(a)



(b)

Fig. 2. Strain-temperature curves under different constant tensile loads obtained for Co–Ni–Ga SIM-aged at 400°C for 20 min (a) and plots of the characteristic transformation temperatures vs. applied stress (b). Following SIM-aging the CC-slope for each transformation temperature is about 0.6 MPa C^{-1}. The corresponding data points were extracted from the strain-temperature curves as indicated by markers for the 125 MPa hysteresis in (a).

The degree of order can be qualitatively deduced from the intensity of superlattice reflection spots of the martensitic phase in TEM micrographs (Fig. 1(c)). Weak superlattice reflections labeled by the white circle in Fig. 1(c) indicate a martensite structure with a very low degree of chemical order. In contrast to mechanically stabilized martensite, diffusively stabilized martensite is characterized by a lower degree of chemical order being indicated by fading superlattice reflection spots.[16,18] Furthermore, from the SAED-pattern (Figs. 1(b) and 1(c)) it is clear that no significant amounts of secondary phases are present and, thus, could not contribute to the stabilization of martensite.

In order to evaluate functional properties of the SIM-aged condition under tensile loads, thermal cycling experiments were performed under different constant tensile stresses (Fig. 2(a)). The heating–cooling cycles for SIM-aged Co–Ni–Ga reveal a fully reversible martensitic phase transformation up to stress levels of 125 MPa. Niendorf *et al.*[28] studied the shape memory behavior for as-grown ⟨001⟩-oriented Co–Ni–Ga single crystals under tensile loads in previous work. For a superimposed tensile stress level of 100 MPa, a M_s temperature of about 60°C was reported.[28] Comparing the as-grown condition to the SIM-aged condition, the increase of the transformation temperatures is apparent (Fig. 2(a)), being in the order of 150°C. As previously discussed, the increase of the transformation temperatures is related to SC-SRO proposed by Ren and Otsuka[19,20] as has been shown for Co–Ni–Ga SIM-aged in compression.[17] The results of the current study confirm that the increase in transformation temperatures is also present for tensile loading conditions. Thus, Co–Ni–Ga HT-SMAs can also operate under conditions of cyclic high-temperature tensile loading.

The evolution of the phase transformation temperatures is summarized in Fig. 2(b). Characteristic temperatures were extracted from the strain-temperature hysteresis in Fig. 2(a) and plotted as a function of the applied stress. The slopes of the four Clausius–Clapeyron (CC) lines are almost identical with values close to 0.6 MPa C^{-1} for each transformation temperature. These values for the SIM-aged condition are only slightly lower as those reported in the literature for as-grown Co–Ni–Ga.[28,30] Thus, the SIM-aging heat treatment primarily affects the transformation temperatures.

In order to address functional stability following SIM-aging under tensile loads, cyclic heating–cooling experiments were conducted. In principle, martensite stabilization induced by SC-SRO is known to be fully reversible.[19,20] In previous studies, the alloys under consideration showed a nearly instantaneous recovery from stabilized martensite to the non-stabilized state after (alloy dependent) dwell times in the austenitic phase.[19,20,26] The stability of transformation temperatures during cyclic heating–cooling experiments was examined during 30 cycles in the SIM-aged condition. Experimental parameters for stress levels and cycle numbers were chosen in line with those in Ref. 17 for better comparability. Figure 3 demonstrates excellent stability, i.e. no shift of transformation temperatures or accumulation of irreversible strain. Thus, functional tensile data are in line with the compression results, which were reported in Ref. 17 for up to 30 cycles.

Compared to other alloy systems, such as Cu-based alloys, this microstructural stability relies on slow ordering kinetics prevalent in the austenitic phase of Co–Ni–Ga alloys, which was already pointed out by Picornell *et al.*[25] and Niendorf *et al.*[17] Note, that the transformation temperatures remain stable starting from the second cycle (Fig. 3). Upon heating in the first cycle, following SIM-aging, the martensite to austenite phase transformation occurs at very high temperatures, i.e. A_s is around 380°C, see inset in

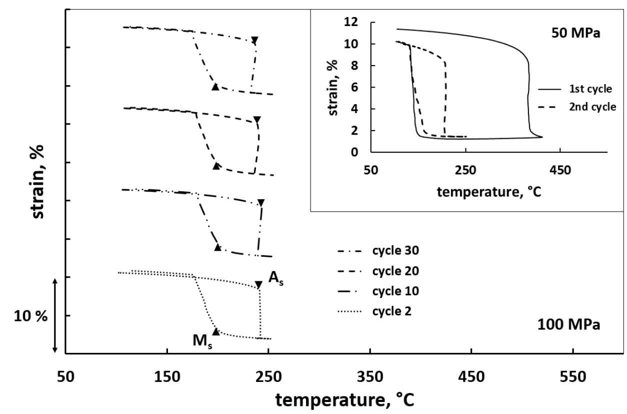


Fig. 3. Cyclic strain-temperature curves under a superimposed tensile stress of 100 MPa for Co–Ni–Ga SIM-aged at 400°C for 20 min. The material showed near perfect cyclic stability up to 30 cycles. The inset shows the first and second cycle following SIM-aging. A significant difference in the A_s values of both cycles is visible, whereas M_s is almost stable from the very first cycle.

Fig. 3. The difference between the A_s values of the first and second cycles after SIM-aging can be attributed to a pinning mechanism induced by point defects exclusively acting in the very first thermal cycle.[17,22] Hence, load increase experiments in Fig. 2(a) as well as thermo-mechanical cycling experiments (Fig. 3) start with the second cycle after SIM-aging. Point defect induced immobilization of martensite phase boundaries does not seem to affect the retransformation since M_s remains stable from the very first cycle on (Fig. 3).

Furthermore, Fig. 3 reveals reversible strains up to 9.5% in the very first cycle qualifying Co–Ni–Ga as a new high performance low-cost HT-SMA. In the last few years, efforts have been made to increase the transformation temperatures of SMAs in order to widen application ranges. The results of

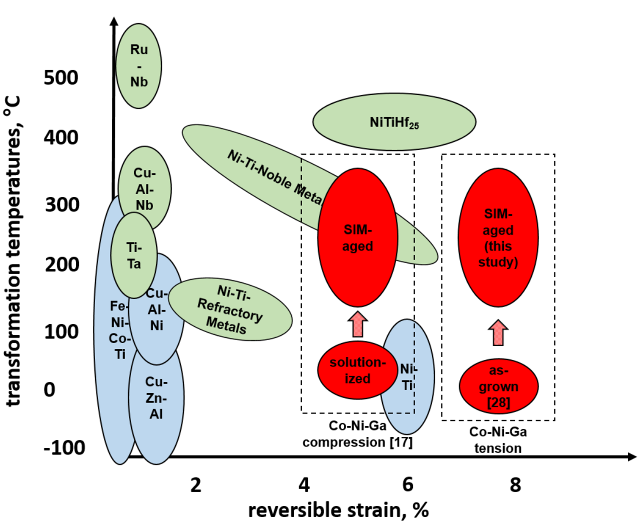


Fig. 4. The schematic illustrates transformation temperatures and reversible strains. The Co–Ni–Ga alloy SIM-aged in compression as well as in tension is compared with conventional (blue) and HT (green) SMAs. The plot is recompiled from Refs. 17, 28 and 31.

the current study for Co–Ni–Ga HT-SMAs contribute to this endeavor (Fig. 4).

In conclusion, in view of the conventional and high-temperature SMAs which have been considered so far, Co–Ni–Ga HT-SMAs represent a new promising alternative. They merit further attention and further research in understanding their properties and tailoring their functional and structural properties seems fully justified.

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References

1. K. Otsuka *et al.*, *Shape Memory Materials* (Cambridge University Press, Cambridge, 1999).
2. K. Otsuka *et al.*, *Prog. Mater Sci.* **50**, 511 (2005).
3. H. Sehitoglu *et al.*, *Curr. Opin. Solid State Mater. Sci.* **21**, 113 (2017).
4. J. Ma *et al.*, *Int. Mater. Rev.* **55**, 257 (2013).
5. D. C. Lagoudas, *Shape Memory Alloys* (Springer, Boston, 2008).
6. Y. Liu *et al.*, *Acta Mater.* **98**, 164 (2015).
7. B. S. Shariat *et al.*, *Mater. Des.* **124**, 225 (2017).
8. Y. L. Hao *et al.*, *J. Mater. Sci. Technol.* **32**, 705 (2016).
9. P. J. S. Buenconsejo *et al.*, *Acta Mater.* **57**, 1068 (2009).
10. P. J. S. Buenconsejo *et al.*, *Acta Mater.* **57**, 2509 (2009).
11. Y. Xin *et al.*, *Mater. Sci. Eng. A* **649**, 254 (2016).
12. G. S. Firstov *et al.*, *J. Intell. Mater. Syst. Struct.* **17**, 1041 (2006).
13. J. Liu *et al.*, *J. Alloys Compd.* **420**, 145 (2006).
14. K. Oikawa *et al.*, *Mater. Trans.* **42**, 2472 (2001).
15. J. Dadda *et al.*, *Scr. Mater.* **55**, 663 (2006).
16. P. Krooß *et al.*, *Shap. Mem. Superelasticity* **2**, 37 (2016).
17. T. Niendorf *et al.*, *Acta Mater.* **89**, 298 (2015).
18. P. M. Kadletz *et al.*, *Mater. Lett.* **159**, 16 (2015).
19. X. Ren *et al.*, *Nature* **389**, 579 (1997).
20. K. Otsuka *et al.*, *Mater. Sci. Eng. A* **312**, 207 (2001).
21. N. M. Bruno *et al.*, *Acta Mater.* **142**, 95 (2018).
22. S. Kustov *et al.*, *Acta Mater.* **52**, 3075 (2004).
23. V. A. Chernenko *et al.*, *Scr. Mater.* **50**, 225 (2004).
24. C. Picornell *et al.*, *Acta Mater.* **49**, 4221 (2001).
25. C. Picornell *et al.*, *Funct. Mater. Lett.* **2**, 83 (2009).
26. A. Abu-Arab *et al.*, *Scr. Metall.* **18**, 709 (1984).
27. J. van Humbeeck *et al.*, *Scr. Metall.* **18**, 893 (1984).
28. T. Niendorf *et al.*, *Mater. Sci. Forum* **738–739**, 82 (2013).
29. J. Dadda *et al.*, *Metall. Mater. Trans. A* **39**, 2026 (2008).
30. J. A. Monroe *et al.*, *Scr. Mater.* **62**, 368 (2010).
31. L. Patriarca *et al.*, *Scr. Mater.* **115**, 133 (2016).