Mechanical Stabilization of Martensite: Comparison of Ni–Mn–Ga and Cu–Ni–Al Shape Memory Single Crystals

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Newly developed formalism, regarding 2H modulated Cu–Ni–Al system as non-magnetic equivalent of Ni–Mn–Ga 10M modulated martensite provides the way to compare behaviour of these two shape memory alloys. Here we study the mechanical stabilization by mechanical stress in the single crystals of $Ni_{50.7}Mn_{27.7}Ga_{21.6}$ (at.%) and $Ni_{46}Mn_{24}Ga_{22}Co_4Cu_4$ exhibiting 10M and non-modulated martensite structures, respectively, and for comparison in $Cu_{69.4}Ni_{3.4}Al_{27.2}$ 2H martensite. The resulting shift of reverse transformation temperature was almost 50 K in the Cu–Ni–Al 2H martensite and about 6 K in Ni–Mn–Ga non-modulated martensite. In contrast, the shift was <1 K in 10M Ni–Mn–Ga martensite. From the comparison it follows that the negligible stabilization in modulated 10M Ni–Mn–Ga can be due to its deep twinning hierarchy and very high mobility of twin boundaries.

1. Introduction

Mechanical stabilization of martensite has been observed in several shape memory alloys such as Ni–Ti, Ni–Ti–Nb, or Cu–Al–Zn–Mn [1–4]. Prominent example is the Cu–Ni–Al alloy in single crystal form [5–7]. The effect is seen as increased reverse martensite transformation temperature in mechanically loaded martensite. The self-accommodated martensite is altered by external stress into different microstructure impairing martensite-austenite compatibility. Restoring the compatible microstructure costs energy and consequently results in the shifted reverse transformation temperature [6].

The shift of transformation temperature after mechanical compression was also observed in Ni–Mn–Ga magnetic shape memory (MSM) alloy [8] but it was not identified as mechanical stabilization. Ni–Mn–Ga constitutes the most application-promising material exhibiting the MSM effects or magnetically induced reorientation (MIR) resulting in up to 12% strain in magnetic field [9, 10]. It was shown that compression stress partially suppresses MIR [11] and there are some studies on the effect of mechanical stress on martensitic transformation in Ni–Mn–Ga 10M martensite [12] but the specific effect of martensite mechanical stabilization was not recognized. Recently, we suggested that Cu–Ni–Al single crystal is a good non-magnetic analog to Ni–Mn–Ga [13] and thus the mechanism of mechanical stabilization can be similar.

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The parent cubic austenite phase has $L2_1$ long-range ordered structure for Ni–Mn–Ga and DO_3 structure for Cu–Ni–Al, which can be considered as degenerate $L2_1$ structure [14, 15]. With decrease in temperature one of the several martensitic phases occurs: non-modulated (NM) martensite, 10M or 14M modulated martensites for Ni–Mn–Ga [9, 10] and 2H or 18R modulated martensites for Cu–Ni–Al [14]. In this study we focus on NM, 10M, and 2H structures.

According to developed formalism [13], both 10M Ni–Mn–Ga and 2H Cu–Ni–Al can be described by monoclinic structure. Twelve different variants are possible in 10M modulated martensite of Ni–Mn–Ga. The highest twin hierarchy with four different types of twins can be observed in 10M Ni–Mn–Ga: compound a-b twin laminate, monoclinic twins, type I and type II twins [9]. In the 2H martensite of Cu–Ni–Al six different variants are possible and they can be connected by compound, type I, and type II twin boundaries [16, 17]. As NM martensite of Ni–Mn–Ga has tetragonal structure there are only three possible variants with compound twinning [18].

Here we compare the mechanical stabilization phenomenon in NM, 10M, and 2H Ni–Mn–Ga and Cu–Ni–Al martensites. These three martensites differ in twinning hierarchy and mobility of twinning boundaries which seems to be the basic elements controlling the stabilization.

2. Experiment

Four single crystals of $Ni_{46}Mn_{24}Ga_{22}Co_4Cu_4$, $Ni_{50}Mn_{28.7}Ga_{21.3}$, $Ni_{50.7}Mn_{27.7}Ga_{21.6}$, and $Cu_{69.4}Ni_{3.4}Al_{27.2}$ (at.%) grown by directional solidification were used for this study. $Ni_{46}Mn_{24}Ga_{22}Co_4Cu_4$

exhibits NM martensite at room temperature. Two single crystals of $Ni_{50}Mn_{28.7}Ga_{21.3}$ and $Ni_{50.7}Mn_{27.7}Ga_{21.6}$ exhibit 10M modulated martensite structure and $Cu_{69.4}Ni_{3.4}Al_{27.2}$ has 2H modulated martensite structure at room temperature. The cuboid single crystals were cut along {100}planes. The mechanical stabilization was performed by mechanical compression along [100] or [001] directions up to $\approx$ 10 MPa in NM and 10M modulated martensites, and up to $\approx$ 100 MPa in 2H Cu–Ni–Al martensite. The reorientation was performed in INSTRON 1362 electromechanical testing machine and by in-house made micrometer screw-based mechanical loading device.

The transformation temperatures of ferromagnetic Ni–Mn–Ga crystals were detected by low-field magnetization measurements using vibrating sample magnetometer PPMS (Quantum Design) at 0.01 T magnetic field with the cooling/heating rate of 4 K/min. The transformation temperatures and latent heat were determined by differential scanning calorimetry (DSC) on all crystals using Linkam Instrument with the cooling/heating rate of 5 K/min. The latent heats were calculated from the area under the transformation peaks and calibrated using Ga sample.

3. Results and discussion

Magnetic susceptibility measurements for Ni–Mn–Ga crystals are shown in Fig. 1. The martensitic transformations are seen as discontinuities in susceptibility due to sharp changes of magnetic anisotropy upon transformation [9, 19]. All transformation temperatures T'_a, T_a and T_m are defined here as a temperature where the sharp changes of the magnetic susceptibility occurs. In the figure the curves for the stabilized state after reorientation by compression are compared with the curves for the self-accommodated state obtained by the transformation to austenite and then back to martensite. Following measurements for the self-accommodated state (not shown) were all very similar indicating the stabilization occurs only in the first cycle and it is wiped out by transformation to austenite. The transformation temperature T'_a for stabilized NM Ni–Mn–Ga was shifted by about 6 K from T_a for the self-accommodated state (Fig. 1a). However, for the 10M Ni–Mn–Ga the shift is less than 1 K (Fig. 1b), which is on the edge of measuring precision.

As the Cu–Ni–Al is not ferromagnetic, DSC was used for all three examined materials. The summary of DSC measurements is shown in Fig. 2. Again the stabilized state after reorientation by compression is compared with the self-accommodated state. Repeated measurements for self-accommodated Ni–Mn–Ga (not shown) were identical in agreement with the magnetic measurements. In contrast, small differences were observed in Cu–Ni–Al crystal. Significant differences, however, were observed between deformed and as-received annealed material without any previous deformation. Transformation back to martensite is similar for all alloys and differently treated samples.
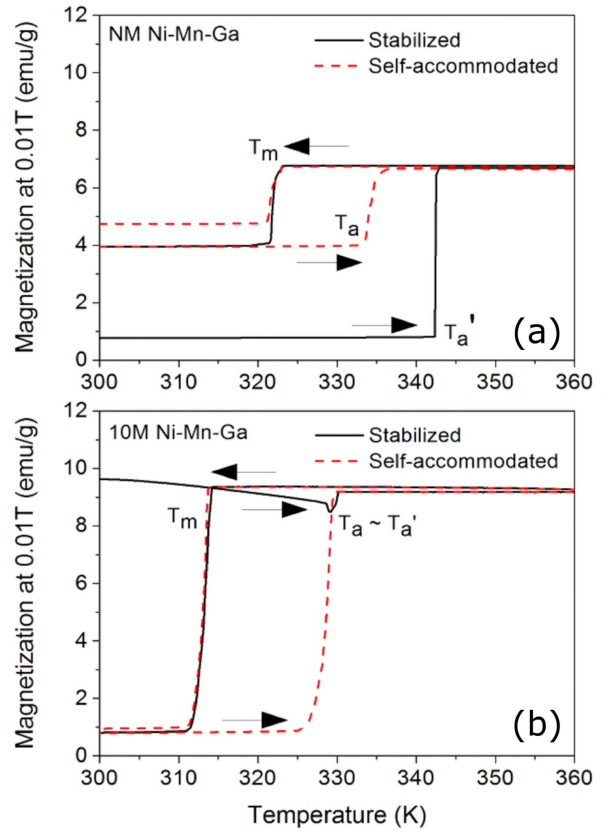

Fig. 1. DC magnetic susceptibility measurements in the field of 0.01 T for (a) NM Ni–Mn–Ga, (b) 10M Ni–Mn–Ga. Solid black line — the stabilized state after reorientation by compression. Dashed red line — the self-accommodated state after transformation to the austenite and then back to the martensite. The transformation temperatures are marked: T_m: austenite to martensite, T_a: martensite to austenite, T'_a: martensite to austenite after stabilization. Cooling/heating rate was 4 K/min.

TABLE I

Transformation temperature difference ΔT between self-accommodated and stabilized state and latent heat of transformations from martensite to austenite.

	ΔT [K]	Latent heat [J/g]	
		self-accommodated	stabilized
10M Ni–Mn–Ga	< 1	11.5	11.5
NM Ni–Mn–Ga	≈ 6	11.0	11.7
2H Cu–Ni–Al	≈ 50	13.7	20.6

In DSC measurements, we determine the transformation temperatures as positions of peak maximum/minimum which is reasonable approximation to determine the stabilization. The transformation temperatures together with latent heat of transformation from martensite to austenite are listed in Table I. It shows that there are large differences between alloys.

Before we discuss the observed difference ascribed to mechanical stabilization, we look on puzzling dif-
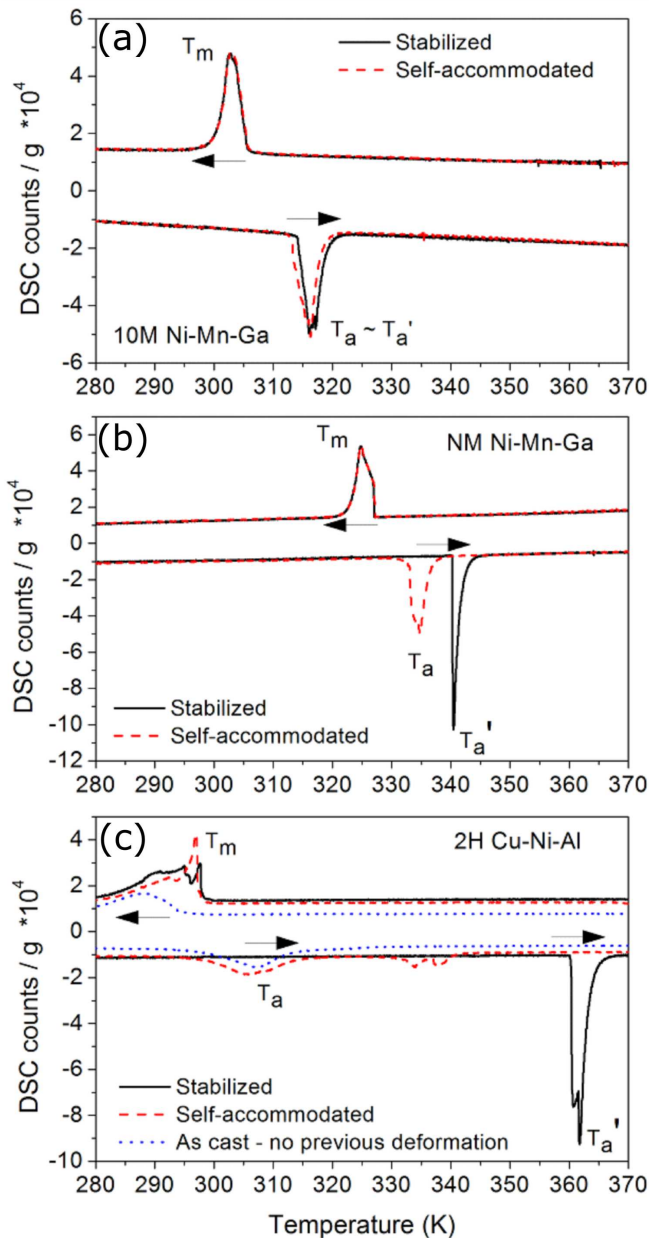
Fig. 2. DSC measurements of (a) 10M Ni–Mn–Ga, (b) NM Ni–Mn–Ga, (c) 2H Cu–Ni–Al. Solid black lines — stabilized state after reorientation by compression. Dashed red lines — self-accommodated state after transformation from austenite. Dotted blue line in (c) — as cast material without any previous deformation. The transformation temperatures are marked: T_m: austenite to martensite transformation, T_a: martensite to austenite, T_a': martensite to austenite after stabilization. Cooling/heating rate was 5 K/min.

ference in transformation behaviour between accommodated state after compression and as-received (i.e without any mechanical load) 2H martensite of Cu–Ni–Al (Fig. 2c). The broadening of the transformation for the material subjected to mechanical deformation was not observed previously as the thermal analysis is usually done first followed by mechanical testing. In this material without any previous deformation as in [13] only single peak occurs (Fig. 2c). In self-accommodated state after initial compression there are two peaks instead of one during the transformation from martensite to austenite. The larger first peak occurs at approximately 305 K coinciding with as-received material followed by a smaller second peak at 335 K. According to X-ray measurements (not shown) the material transforms gradually to the austenite in the whole temperature interval from 305 K to 335 K. Also latent heat in these two cases is similar. Thus both peaks can be ascribed to a single gradual transformation with low activity in the middle region.

Observed difference indicates that even single mechanical loading in 2H martensite creates some irreversible structural changes. The second peak on the DSC curve may be explained by sudden releasing of the last pinned corners of martensite indicated by the increase of acoustic emission activity [7]. The structural changes induced by compression also slightly increase the transformation temperature from austenite to martensite and make the transformation sharper (Fig. 2c).

Apart of the shift of temperature due to mechanical stress, it can be seen from the DSC curves (Fig. 2b,c) that the peaks for stabilized state of NM Ni–Mn–Ga and 2H Cu–Ni–Al are sharper and higher than peaks for self-accommodated state or as-received state in Cu–Ni–Al. This indicates that when increased nucleation barrier for transformation due to stabilization is reached the transformation occurs faster and in much smaller temperature interval. However, the DSC peaks for stabilized and self-accommodated state in 10M Ni–Mn–Ga have the same shape (Fig. 2a) indicating negligible stabilization in 10M Ni–Mn–Ga.

The latent heat for NM Ni–Mn–Ga and 2H Cu–Ni–Al is higher for stabilized state with differences between the self-accommodated and stabilized state being about 7% for NM Ni–Mn–Ga and 30% for 2H Cu–Ni–A. There is no difference for 10M state. The differences are in agreement with the highest stabilization in 2H Cu–Ni–Al, intermediate effect in NM, and negligible stabilization in 10M Ni–Mn–Ga.

According to [6, 7, 20], to secure the compatibility between martensite and austenite the interfacial microstructure is formed during transformation from austenite to martensite. After mechanical loading this interfacial microstructure is wiped out. Following transformation to austenite cannot occur before some interfacial microstructure is re-established. The formation of interfacial microstructure can be imagined as additional nucleation, twinning and formation of laminate of differently oriented variants to secure compatibility on habit plane [6, 7]. Apparently better compatibility can be achieved if more twinning systems are available and thus it is no surprise that negligible stabilization occurs in 10M.

However, the stronger stabilization of 2H Cu–Ni–Al by comparison to NM Ni–Mn–Ga indicates that the amount

of possible twinning systems is not a critical element. Only one type of twinning which can form only 3 different variants in NM Ni–Mn–Ga does not cause a higher stabilization than three possible types of twinning in 2H Cu–Ni–Al which produces 6 variants.

Our experiment suggests that for nucleation and propagation of interfacial microstructures the twinning mobility is more important. The twinning stress for compound twinning in NM Ni–Mn–Ga is approximately 10 times lower than the twinning stress for type II twinning in 2H Cu–Ni–Al, which also roughly corresponds to the amount of stabilization of these two alloys (temperature shift in NM Ni–Mn–Ga is roughly 10 times lower). Almost no stabilization in 10M Ni–Mn–Ga (< 1 K) is in agreement with the very high mobility of twin boundaries with the twinning stress about 0.2 MPa [21, 22]. Results of stabilization of these three materials suggest linear dependence between the stabilization and the mobility of twin boundaries. Furthermore, deep twin hierarchy unique for 10M Ni–Mn–Ga [23] may further facilitate reaching the compatibility. This agrees with observation that DSC peaks in the stabilized (by stress) and self-accommodated state in 10M Ni–Mn–Ga have the same shape, which indicates that the compatibility between martensite and austenite is not changed dramatically by changing twin microstructure by stress.

4. Conclusions

Developed formalism allows full comparison of the single crystals of Ni–Mn–Ga and Cu–Ni–Al [13]. The stabilization of martensite caused the biggest shift (almost 50 K) of the reverse transformation temperature in 2H modulated Cu–Ni–Al. The shift of the transformation temperature in NM modulated Ni–Mn–Ga was approximately 6 K and the lowest shift < 1 K was found in 10M modulated Ni–Mn–Ga. The main reason for almost no stabilization in modulated 10M Ni–Mn–Ga is its deep twinning hierarchy and very highly mobile twin boundaries, which can easily form the interfacial microstructure needed for kinematic compatibility. The comparison of stabilization in 2H Cu–Ni–Al and NM Ni–Mn–Ga suggests that the mobility of twin boundaries is more important factor for stabilization than the amount of possible twinning systems.

Acknowledgments

References

[1] M. Piao, K. Otsuka, S. Miyazaki, H. Horikawa, *Mater. Trans. JIM* **34**, 919 (1993).

[2] Y. Liu, D. Favier, *Acta Mater.* **48**, 3489 (2000).

[3] Y. Liu, Y. Liu, J. Van Humbeeck, *Acta Mater.* **47**, 199 (1999).

[4] C. Picornell, J. Pons, E. Cesari, *Acta Mater.* **49**, 4221 (2001).

[5] C. Picornell, V.A. L'vov, J. Pons, E. Cesari, *Mater. Sci. Eng. A Struct. Mater. Prop. Microstruct. Process.* **438**, 730 (2006).

[6] H. Seiner, P. Sedlak, M. Landa, *Phase Transit.* **81**, 537 (2008).

[7] H. Seiner, *Shap. Mem. Superelast.* **1**, 268 (2015).

[8] E. Pagounis, M.J. Szczerba, R. Chulist, M. Laufenberg, *Appl. Phys. Lett.* **107**, 152407 (2015).

[9] O. Heczko, N. Scheerbaum, O. Gutfleisch, in: *Nanoscale Magnetic Materials and Applications*, Ed. J.P. Liu, Springer Science+Business Media, New York 2009, p. 399.

[10] O. Heczko, *Mater. Sci. Technol.* **30**, 1559 (2014).

[11] K. Richterová, J. Drahokoupil, V. Kopecký, K. Dragounová, M. Landa, O. Heczko, *Acta Phys. Pol. A* **128**, 704 (2015).

[12] L. Straka, O. Heczko, V. Novák, N. Lanska, *J. Phys. IV (France)* **112**, 911 (2003).

[13] M. Vronka, H. Seiner, O. Heczko, *Philos. Mag.* **97**, 1479 (2017).

[14] V. Novak, P. Sittner, S. Ignacova, T. Cernoch, *Mater. Sci. Eng. A Struct. Mater. Prop. Microstruct. Process.* **438**, 755 (2006).

[15] R.W. Overholser, M. Wuttig, D.A. Neumann, *Scr. Mater.* **40**, 1095 (1999).

[16] K. Bhattacharya, *Microstructure of Martensite: How It Forms and How It Gives Rise to the Shape Memory Effect*, Oxford University Press, Oxford 2004.

[17] U. Sari, I. Aksoy, *J. Alloys Comp.* **417**, 138 (2006).

[18] A. Sozinov, A. Soroka, N. Lanska, M. Rameš, L. Straka, K. Ullakko, *Scr. Mater.* **131**, 33 (2017).

[19] L. Straka, O. Heczko, *J. Appl. Phys.* **93**, 8636 (2003).

[20] H. Seiner, O. Glatz, M. Landa, *Int. J. Multiscale Comp. Eng.* **7**, 445 (2009).

[21] L. Straka, O. Heczko, A. Sozinov, *Acta Mater.* **59**, 7450 (2011).

[22] D. Kellis, A. Smith, K. Ullakko, P. Müllner, *J. Cryst. Growth* **359**, 64 (2012).

[23] H. Seiner, L. Straka, O. Heczko, *J. Mech. Phys. Solids* **64**, 198 (2014).