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# Inter-martensite strain evolution in NiMnGa single crystals

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### 9 Abstract

10 Stress-induced martensitic transformations are clarified in classes of NiMnGa alloys which undergo the stress-free, thermal-induced inter-martensite transformation austenite (A)  $\rightleftharpoons$  pre-martensite (PM)  $\rightleftharpoons$  martensite. This study implements a comprehensive experi-11 mental approach, including analysis of the strain-temperature and stress-strain response, which discloses stress-induced inter-martensite 12 13 transitions. The evolution of the transitions is elucidated using in situ digital image correlation (DIC) measurements of meso-scale strain 14 fields. Under stress, this body of work unequivocally demonstrates that the transformation path becomes  $A \Rightarrow PM \Rightarrow I \Rightarrow 10M$ . The I-15 phase is an intermediate stress-induced martensite with a modulation period between three and five-layers. Owing to the intermediate 16 transition, the thermal hysteresis in the strain-temperature response is tiny (<10 °C) compared with the hysteresis (32 °C) for 17 A = 10M. The differential hysteresis levels are rationalized based on a thermo-mechanical formulation. Meso-scale DIC measurements 18 quantify inter-martensite strain levels, which are indistinguishable from macro-scale stress-strain and strain-temperature responses. 19 © 2008 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

20 *Keywords:* Digital image correlation; Compression test; Strain vs. temperature; Thermal hysteresis; Metastable phases 21

### 22 **1. Introduction**

Shape memory alloys (SMA) undergo a reversible mar-23 tensitic transformation (MT) during constant load temper-24 ature cycling and constant temperature load cycling. 25 Classes of SMA designated ferromagnetic shape memory 26 27 alloys (FSMA) exhibit magnetic field induced strains in the martensitic state. NiMnGa alloys are classes of FSMA 28 that have attracted attention mainly due to promising mag-29 netic field induced strains [1,2]. Reports on the stress-strain 30 response at constant temperature show that these alloys 31 recover strains above 10% and exhibit stress hysteresis 32 from 10 to 100 MPa [3], making them good candidates 33 for non-magnetic SMA applications. NiMnGa alloys with 34 35  $M_{\rm s}$  temperatures near or below -73 °C undergo a thermalinduced transformation austenite  $(A) \rightleftharpoons$  pre-martensite 36  $(PM) \rightleftharpoons$  martensite (M) without stress [4]. Narrow ther-37

Q1 \* Corresponding author. Tel.: +1 217 333 4112; fax: +1 217 244 6534. *E-mail address:* huseyin@uiuc.edu (H. Sehitoglu). mal hysteresis has been reported for the initial transforma-38 tion  $A \rightleftharpoons PM$  (~3 °C) and the subsequent inter-39 martensitic transition PM  $\Rightarrow 10M$  (~10 °C) [5,6]. The 40 number of published reports on the transformation under 41 stress and the accompanying hysteresis is insufficient [7-42 9]. Of these reports, only Kokorin et al. [7] consider con-43 stant load thermal cycling. The current work expounds 44 on the stress-induced transformation using constant load 45 thermal cycling at increasing compressive stress levels for 46 the first time. 47

To characterize the PM phase, Zheludev et al. [10,11] 48 study neutron scattering measurements of the  $[\zeta \zeta 0]$  TA<sub>2</sub> 49 phonon dispersion curves. For the 10M structure, which 50 exhibits five-layer modulation, the  $\zeta = \zeta_M = 0.43$ . They 51 characterize the PM as a modulation of the austenite crys-52 tal structure  $(L2_1)$  with displacements along  $(1\overline{1}0)$  that cor-53 responds to  $\zeta = \zeta_0 = 0.33$ . Under stress,  $\zeta_0$  increases to 0.36 54 at 95 MPa [11]. From the work of Zheludev and his col-55 leagues, we understand that the modulation of stress-56 induced intermediate martensite is sensitive to stress. More 57

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recently, the PM has been identified as three-layer modu-58 lated martensite [12]. This study investigates the alloy com-59 position Ni<sub>48 4</sub>Mn<sub>27</sub>Ga<sub>24 6</sub>, which undergoes the unstressed 60 thermal-induced transformation  $A \rightleftharpoons PM \rightleftharpoons 10M$ . To 61 62 elucidate the transformation path under stress, this work presents an original in situ digital image correlation 63 64 (DIC) analysis of meso-scale transformation strains during load cycling at a constant temperature and constant load 65 temperature cycling. 66

The transformation path during constant load tempera-67 ture cycling is unclear in the literature for NiMnGa alloys 68 that undergo the unstressed thermal-induced  $A \rightleftharpoons$ 69  $PM \Rightarrow 10M$  transformation. Kim et al. [8] report the 70  $A \rightleftharpoons PM \rightleftharpoons PM$  in [001] oriented single crystals; where 71 the X-phase is a stress-induced intermediate phase of 72 unknown crystal structure. Remarkably, they report the 73 opposite inter-martensitic transition  $PM \rightleftharpoons X$  for the 74 stress-strain case and provide no explanation for the dis-75 crepancy. Kokorin et al. [7], in contrast, do not report an 76 intermediate transition prior to the PM phase. They denote 77 78 the pre-martensite phase I and report the transformation 79 path  $A \rightleftharpoons I \rightleftharpoons M$ . The martensite (M) structure is not 80 reported. From the authors' constant load temperature cycling study, it is unequivocally ascertained that the 81  $A \rightleftharpoons PM \rightleftharpoons 10M$  transformation becomes  $A \rightleftharpoons PM \rightleftharpoons$ 82  $I \rightleftharpoons 10M$  with increasing stress. Here, the I-phase is a 83 stress-induced intermediate phase different from PM. From 84 85 the findings of Zheludev and his colleagues, the modulation should be between three-layers and five-layers for the I-86 87 phase in the current Ni<sub>48.4</sub>Mn<sub>27</sub>Ga<sub>24.6</sub> alloy.

Unprecedented two-stage strain-temperature responses 88 measured during constant load temperature cycling are 89 presented. The first stage commences with the  $A \rightleftharpoons PM$ 90 91 transformation. Meso-scale in situ DIC strain measurements expose that the inter-martensitic transformation 92 93  $PM \Rightarrow I$  transformation takes place as well. The second stage is attributed to I  $\rightleftharpoons$  10*M*. The A  $\rightleftharpoons$  PM  $\rightleftharpoons$  I trans-94 95 formation produces a thermal hysteresis  $\sim 1 \,^{\circ}\text{C}$  and the  $I \Rightarrow 10M$  transition results in a thermal hysteresis 96 <10 °C. The narrow hysteresis is rationalized based on a 97 thermo-mechanical formulation. In the stress-strain case, 98 as the temperature is raised, the response changes from 99 100 two stages (i.e., two plateau stresses) to a single stage. An outstanding finding from the in situ DIC technique is that 101 the inter-martensitic transformation  $A \rightleftharpoons I \rightleftharpoons 10M$  per-102 103 sists when a single plateau is observed. Ultimately, the results underscore that implementing in situ DIC to study 104 the evolution of meso-scale strain fields in stress-strain 105 and strain-temperature responses is a novel approach to 106 investigating inter-martensitic phase transitions. 107

### 108 **2. Material and experimental methods**

The alloy was cast to the nominal composition Ni<sub>48.4</sub>Mn<sub>27.0</sub>Ga<sub>24.6</sub> (at.%). Single crystal ingots were grown using the Bridgman technique. Compression  $(4 \times 4 \times 10 \text{ mm}^3)$  specimens were electro-discharge machined from the ingots such that loading is along the [001] orientation 113 with the side faces parallel to the (100) plane. To charac-114 terize the unstressed MT, heat flow was measured as a 115 function of temperature using a Perkin Elmer Pyris 1 differ-116 ential scanning calorimeter (DSC). Two peaks were 117 observed in the cooling (forward MT) and heating (reverse 118 MT) thermo-grams. The first and second peaks start at 119 -34 and -95 °C, respectively, and the corresponding ther-120 mal hysteresis are 5 and 15 °C. Furthermore, the latent 121 heat of transformation for the second peak is twice that 122 of the first. The larger transformation hysteresis and latent 123 heat for the second peak are indicative of the MT. Trans-124 mission electron microscopy reveals that the predominant 125 martensitic phase is 10*M*. For the first peak, which exists 126 at the higher temperature, a thermal-induced pre-martens-127 itic transformation (PM) takes place. The PM is typically 128 observed for NiMnGa alloys that undergo MTs below 129 -73 °C [4]. Planes et al. [6] report differential hysteresis 130 and latent heat measurements for the PM and MT compa-131 rable with those observed here. With this, the stress-free 132 thermal-induced transformation is  $A \rightleftharpoons PM \rightleftharpoons 10M$  in 133 the current Ni<sub>48</sub> 4Mn<sub>27</sub> 0Ga<sub>24</sub> 6 alloy. 134

Mechanical loading experiments were conducted on an 135 Instron servo-hydraulic load frame. Isothermal load 136 cycling experiments were conducted under position con-137 trol. For temperature cycling, the specimens were enclosed 138 in an insulated environment. The specimen was cooled and 139 heated via conduction; the grips were cooled and heated 140 using liquid nitrogen and an induction heater. A thermo-141 couple was welded to the specimen to measure the temper-142 ature, and scan rates were approximately  $\pm 10$  °C min<sup>-1</sup>. 143 Macro-scale strain was measured with a miniature exten-144 someter with a 3 mm gauge length. Within the gauge 145 length, meso-scale strains were calculated using a full-field 146 optical measurement technique called DIC. For DIC anal-147 ysis, the specimen surface was polished and a speckle pat-148 tern was spray painted onto it. In situ images of the 149 specimen surface were captured with an IMI model 150 IMB-202FT ( $1600 \times 1200$  pixels) and Sony XCD-sx900 151  $(1280 \times 960 \text{ pixels})$  CCD cameras. Image acquisition was 152 programmed into the mechanical testing software, which 153 is based on National Instruments LabVIEW. Displace-154 ments were measured by tracking the evolution of the 155 speckle pattern. The strains were calculated from the dis-156 placement gradients. Image correlation and subsequent 157 strain calculations were achieved using software developed 158 by Correlated Solutions (www.correlatedsolutions.com). 159

### **3.** Experimental results

#### 3.1. Compressive strain-temperature response

For constant stress-temperature cycling, compressive 162 stress magnitudes are monotonically increased from 3 to 163 100 MPa. Representative strain-temperature  $(\epsilon - T)$  164 responses are included in Fig. 1. At each stress level, the 165 final martensite product is 10*M* structure based on TEM 166

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Fig. 1. Compressive strain-temperature responses. Single and double arrows mark cooling and heating curves, respectively. The 10*M* is the final martensite structure, and the corresponding thermal hysteresis is designated  $\Delta T_{m(10M)}$ . At -40 and -100 MPa, two stages are evident. In the first stage, the A denotes austenite, PM denotes pre-martensite, and I denotes an intermediate stress-induced phase.

167 analysis. The cooling  $\varepsilon$ -*T* curve becomes vertical as the 168 material transforms to the 10*M* structure. Specifically, the 169 transition to the 10*M* structure starts and ends at the same 170 temperature. Prior to the vertical segment, the curve is non-171 linear at -10 MPa; however, there is a sharp corner at 172 -20 MPa. It will be rationalized that this contrast marks 173 a change in the transformation path.

At -40 to -100 MPa, the  $\varepsilon$ -T responses exhibit two dif-174 ferent slopes, which evidence a two-stage transformation. 175 The first stage starts at  $M_{\rm s} \approx -28$  °C. The temperature is 176 close to the stress-free start temperature  $M_{s(PM)} = -34$  °C, 177 and thus, the  $A \rightarrow PM$  commences. Note that the increase 178 in  $M_s$  is expected owing to the application of stress. The 179 first stage proceeds over a broad temperature range 180 181  $(\sim 50 \text{ °C})$ , which is markedly different from the nearly isothermal second stage. To shed light on the transformation 182 path for the two-stage case, the evolution of meso-scale 183 strain fields is studied using in situ DIC. 184

## 185 3.2. In situ DIC: strain-temperature response

In situ DIC strain field measurements at -10 and 186 187 -40 MPa are shown in the inset images in Figs. 2 and 3, respectively. Successive images are captured during cool-188 ing, and selected images are presented in the figures. In 189 Fig. 2, the strain fields are shown for the  $\varepsilon$ -T response at 190 -10 MPa. Within the initial image, the strain field is pri-191 marily 0%. An arrow points to a region of non-zero strain. 192 Considering that the image is taken at -74 °C and this 193 temperature is below the stress-free  $M_{s(PM)} = -34$  °C, ther-194 195 mal-induced, self-accommodated groups of multiple PM 196 variants can exist within the microstructure. The selfaccommodated arrangement will inherently minimize 197 198 strain energy and, thus, a nil strain field is evident in the ini-



Fig. 2. Compressive strain-temperature response at -10 MPa. In situ strain fields are included, which are measured using DIC. Strain fields are reported during cooling, and circles along the cooling curve mark where the image is captured.



Fig. 3. Compressive strain-temperature response at -40 MPa showing illustrating the two-stage transformation path. In situ DIC strain fields show the meso-scale strain evolution throughout the first stage. In the text, the authors rationalize the nucleation of PM and the stress-induced I-phase prior to the transformation to 10M.

tial image. A finite volume fraction of austenite remains 199 untransformed with a null field as well, which will be 200 explained on considering in situ DIC measurements at 201 -40 MPa. The region of non-zero strain is attributed to 202 the reorientation of a finite volume fraction of self-accom-203 modated PM into a single variant. The mixture of austenite 204 and PM converts to the 10M structure upon further 205 cooling. 206

DIC strain field measurements at -40 MPa are shown in Fig. 3. The matrix is initially austenitic, i.e., zero strain field. Recall that the start temperature for the first stage implies that the A  $\rightarrow$  PM transformation commences. From the second and third images, a larger volume fraction

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Fig. 4. Compressive stress-strain responses at -60 and -70 °C showing two stress plateaus, which evidence a two-stage transformation path. In situ DIC strain images are included at -60 °C. Based on the evolution of the meso-scale strain fields, the pre-existing, self-accommodated PM phase reorients and de-twins at the first stage. During the second stage, an intermediate martensite phase (I) is stress-induced from PM, which then converts to the 10M phase.

of PM phase reorients into a single variant, which most 212 likely de-twins at the higher load. Also, null fields exist 213 214 within the images. It is anticipated that these fields correspond to untransformed austenite that exists below 215  $M_{\rm f(PM)} \approx -39$  °C. Note that these null fields cannot corre-216 spond to self-accommodated PM. This is because at 217 218 -40 MPa, self-accommodated PM would deform and produce measurable strain, as the stress level exceeds the max-219 imum stress required to reorient and de-twin self-220 accommodated PM, which is approximately -30 MPa at 221 222 -60 °C in Fig. 4. In Fig. 3, a conspicuous band appears 223 near the top of the third image, in which strain levels approach -2%. In situ DIC for the stress-strain response 224 will show that a stress-induced intermediate phase (I-225 phase) reaches a maximum strain of nearly -2%; hence, 226 the green<sup>1</sup> band within the third image in Fig. 4 represents 227 O2 228 the I-phase. The PM phase reaches a maximum strain of -0.75% prior to converting to the I-phase. For regions of 229 -0.75% strain (yellow contours), the PM phase exists. 230 Therefore, the  $A \rightleftharpoons PM \rightleftharpoons I$  transformation is stress-231 induced in the first stage of the  $\varepsilon$ -T response. The second 232 stage is attributed to  $I \Rightarrow 10M$ , and the strain is nearly 233 234 -4%.

At -10 (Fig. 2) and -40 MPa (Fig. 3), the images for 235 the 10M phase do not exhibit uniform strain fields. The 236 heterogeneous local strain fields can imply multiple inter-237 face transformations. This finding is remarkable because 238 239 the cooling  $\varepsilon$ -T curve is isothermal, which typically implies a single interface transformation in single crystals [13]. The 240 isothermal transformation is rationalized in the discussion. 241

### 3.3. In situ DIC: stress-strain response

Representative stress-strain  $(\sigma - \varepsilon)$  responses in the tem-243 perature (T) range  $-70 \leq T \leq -50$  °C are shown in 244 Fig. 4. This range is between the stress-free reverse trans-245 formation temperatures for PM  $\leftarrow 10M$  ( $A_{f(10M)} \approx$ 246 -80 °C) and A  $\leftarrow$  PM ( $A_{\rm f(PM)} \approx -30$  °C) determined from 247 the DSC analysis. Within this temperature range, the 248 matrix will contain the PM phase. Recall that the in situ 249 DIC study of the  $\varepsilon$ -T response (Fig. 3) revealed that a finite 250 volume fraction of material will retain the untransformed 251 austenite structure. Likewise, the matrix consists of austen-252 ite and self-accommodated PM in the range  $-70 \leq T \leq$ 253 -50 °C. The  $\sigma$ - $\varepsilon$  response at -60 °C exhibits two stress pla-254 teaus which are indicative of a two-stage transformation. 255 Selected DIC strain-fields are shown during loading. 256 Notice that the critical stress for the first stage decreases 257 with increasing temperature. The opposite trend is expected 258 for the first-order transition  $A \Rightarrow PM$ ; therefore, the first 259 stage is attributed to reorientation and de-twinning of 260 pre-existing self-accommodated PM domains. Note that 261 the maximum strain level is -0.75%, similar to the maxi-262 mum level observed for the PM phase in the  $\varepsilon$ -T response. 263 The strain fields within the second image (Fig. 4) exhibit 264 striking contrasts and are predominantly -2%. Because 265 the critical stress is exceeded prior to the drastic strain evo-266 lution, an intermediate (I-phase) is stress-induced. Through 267 the plateau, the I-phase converts to 10M and the strain 268 fields within final image evidence a mixture of the two 269 phases. Notice that the I-phase began to nucleate in the 270 first image. The same location in the second image exhibits 271 strain fields that evidence the 10M phase. From this DIC 272 analysis, one gleans that the first and second plateaus, 273 respectively, manifest the A  $\Rightarrow$  PM and PM  $\Rightarrow$  I  $\Rightarrow$  10M 274 transformation paths in this Ni<sub>48.4</sub>Mn<sub>27</sub>Ga<sub>24.6</sub> alloy. 275

At T > -50 °C, the  $\sigma - \varepsilon$  curves exhibit a single plateau, 276 which is demonstrated in Fig. 5. At these temperatures, 277



Fig. 5. Compressive stress-stain response at +25 °C showing a single stage. The evolution of meso-scale in situ DIC strain fields exposes that the inter-martensitic transformation  $A \rightleftharpoons I \rightleftharpoons 10M$  takes place.

<sup>&</sup>lt;sup>1</sup> For interpretation of color in Fig. 4, the reader is referred to the web version of this article.

the matrix will have a stabilized austenitic structure 278 279 because they are much higher than the stress-free  $A_{\rm f(PM)} \approx -30$  °C. To ensure DIC analysis is performed in 280 the austenitic state, images are captured at +25 °C. Indeed, 281 282 the first image in Fig. 5 exhibits a homogeneous austenite structure based on the uniform zero strain field. Near the 283 284 transformation stress -300 MPa (measured as the deviation from linearity), the I-phase begins to nucleate within 285 the second image; an arrow marks a strain measurement 286 that reaches -2%. Once the transformation stress is 287 exceeded, the strain fields in the last image reflect that the 288 I-phase is predominant. Furthermore, bands of 10M mar-289 tensite form which achieve strain levels of -3.5%. The 290 value exceeds the macro-scale strain measurement by 1%. 291 The results show that the inter-martensitic transformation 292  $A \rightleftharpoons I \rightleftharpoons 10M$  takes place despite the absence of multiple 293 294 stress plateaus.

### 295 4. Discussion

For the Ni<sub>48.4</sub>Mn<sub>27</sub>Ga<sub>24.6</sub> alloy studied in this work, the 296 297 stress-free thermal-induced transformation is  $A \rightleftharpoons$  $PM \Rightarrow 10M$ . The PM is a micro-modulated phase with a 298 299 3M structure [5–7,11,12,14]. Zheludev et al. [10] and Planes et al. [5,6] envisage that PM and austenite can coexist after 300 the initial transformation. The current in situ DIC analysis 301 during thermal cycling at constant stress (Figs. 2 and 3) 302 illustrates that this is indeed the case. and only a fraction 303 of the austenite undergoes the  $A \rightleftharpoons PM$ . Based on this 304 finding, the initial microstructure is composed of austenite 305 and self-accommodated PM when the  $\sigma$ - $\varepsilon$  responses exhibit 306 two plateaus at temperatures between the stress-free  $A_{\rm f}$ 307 temperatures for  $PM \leftarrow 10M$  and  $A \leftarrow PM$  (Fig. 4). The 308 two plateaus evidence a two-stage transformation. The ini-309 tial stage is attributed to reorientation and de-twinning of 310 pre-existing self-accommodated PM domains. Further-311 more, the macro-scale strain levels achieved throughout 312 313 the initial stage decrease with increasing temperature, because less self-accommodated PM exists at higher tem-314 peratures. From the evolution DIC strain fields, a stress-315 induced inter-martensitic transition  $PM \rightarrow I$  is observed 316 within the second stage at the highest critical stress 317 318 (Fig. 4). The I-phase is a stress-induced intermediate phase, 319 which transforms to 10M during the second stage. Using the in situ DIC technique, the authors have clarified the 320 321 transformation path for two-stage  $\sigma$ - $\varepsilon$  response. Specifically, contrary to Kim and his colleagues' [8] report that 322 attributes the first stage to the stress inducement of an X-323 324 phase, the first stage corresponds to reorientation and detwinning of PM. In the following, this original study of 325 326 the strain-temperature  $(\varepsilon - T)$  response for this class of NiMnGa alloys is discussed. 327

The  $\varepsilon$ -*T* response changes from one (A  $\rightleftharpoons$  10*M*) to two (A  $\rightleftharpoons$  PM  $\rightleftharpoons$  I and I  $\rightleftharpoons$  10*M*) stages with increasing stress (Fig. 1). At each stress level, the forward transformation to the 10*M* starts and ends at the same temperature, and thus the transformation is isothermal. The temperature

interval during the forward MT is related to stored elastic 333 strain energy; a wide interval implies more energy is stored 334 [13,15]. As a single interface propagates in single crystalline 335 alloys, no constraint is imposed on interface motion by 336 grain boundaries or neighboring martensite variants. 337 Therefore, the shape change takes place freely as the single 338 interface traverses the single crystal, and no elastic strain 339 energy is stored [13,15]. For the Ni<sub>48,4</sub>Mn<sub>27</sub>Ga<sub>24,6</sub> alloy, 340 however, DIC strain images captured at the end of the iso-341 thermal cooling  $\varepsilon$ -T segment (Figs. 2 and 3) suggest that 342 multiple interfaces can exist. If a single interface had tra-343 versed the imaged area, a homogeneous strain field should 344 exist [16]. Because this is not the case, the strain fields in 345 Figs. 2 and 3 most likely indicate that multiple interfaces 346 exist. Apparently, the habit plane, the undistorted plane 347 between the I and 10M phases, must be created easily, 348 and thus, the level of stored strain energy is inconsequen-349 tial. To the contrary, substantial strain energy is stored 350 for the first transformation  $(A \rightleftharpoons PM)$  in the two-stage 351  $\varepsilon$ -T responses (-40 and -100 MPa). This is based on the 352 wide transformation temperature range ( $\sim 50$  °C). Strain 353 energy storage is significant because it builds up by contri-354 butions from both the A  $\rightleftharpoons$  PM and PM  $\rightleftharpoons$  I transforma-355 tions (Fig. 3). 356

For the  $A \Rightarrow PM \Rightarrow I$  inter-martensitic transformation, the heating and cooling  $\varepsilon$ -*T* curves overlap at -40 MPa and a tiny thermal hysteresis (<1 °C) exists. At -100 MPa (Fig. 1), though the  $\varepsilon$ -*T* curves do not overlap, the thermal hysteresis is still small; the hysteresis measured  $A_f$ - $M_s$  is <1 °C. Furthermore, the transition to the 10*M* exhibits a smaller hysteresis when it is stress-induced from the I-phase at compressive stress magnitudes -40 and -100 MPa (Fig. 1); the thermal hysteresis  $\Delta T_{m(10M)} \approx 12$  °C is narrower than that measured at -10 MPa ( $\Delta T_{m(10M)} = 21$  °C). The differential hysteresis levels are rationalized in the following based on a thermo-mechanical formulation outlined in previous work [17,18].

An expression for the thermal hysteresis has been derived [18]:

$$\Delta T_{\rm h} = A_{\rm f} - M_{\rm s} = (F_{\rm C(R)} + F_{\rm C(F)})/|\Delta s|$$
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 $F_{C(R)}$  and  $F_{C(F)}$ , respectively, represent the dissipative po-374 tential for the reverse and forward transformation [17].  $F_{\rm C}$ 375 is related to the frictional work that must be overcome for 376 interfacial motion [19].  $|\Delta s|$  is the magnitude of the entropy 377 change for the MT and  $\Delta s = Q/T_0$ , where the latent heat Q 378 equals the area under a DSC peak divided by the tempera-379 ture scan rate. The equilibrium temperature  $T_0$  is estimated 380 as half the sum of the cool and heat peak temperatures. A 381 small change implies a small  $F_{\rm C}$ , and thus will facilitate a 382 narrow hysteresis and vice versa. For the pre-martensite 383 and 10*M* phases, respectively, the  $|\Delta s| = 0.0034$  and 384 0.0138 J (g °C)<sup>-1</sup>. Based on this result, the A  $\rightleftharpoons$  PM facili-385 tates the narrow thermal hysteresis for the first stage. 386

The hysteresis for the transition to 10M becomes narrow for the two-stage transformation compared with the A  $\rightleftharpoons$ 10M (compare -10 and -40 MPa in Fig. 1). In this case,

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390 the forward and reverse transformations correspond to  $I \rightleftharpoons 10M$ . The  $|\Delta s|$  for this transformation is likely lower 391 than that for  $A \rightleftharpoons 10M$ : considering that, the habit plane 392 between I and 10M the phases should be created easily. 393 Moreover, because the I-phase is stress-induced, it will be 394 unstable and I  $\Rightarrow$  10M will experience a lower  $F_{\rm C}$ . These 395 396 two factors promote the shrinking hysteresis  $\Delta T_{m(10M)}$  in 397 Fig. 1. In addition, the elastic strain energy stored during the  $A \rightleftharpoons PM \rightleftharpoons I$  transformation facilitates the smaller 398 hysteresis. The energy assists the reverse transformation 399 enabling it to start closer to  $A_{\rm f}$  (compare Figs. 2 and 3) 400 [17]. Remarkably, for the  $\varepsilon$ -T response at -20 MPa 401 (Fig. 1) the hysteresis is the smallest  $\Delta T_{m(10M)} = 8.5$  °C. 402 Based on the narrow hysteresis, the  $A \rightleftharpoons PM \rightleftharpoons I$  may 403 be facilitated initially, despite the absence of multiple 404 stages. Note that this is substantiated by the abrupt start 405 to the MT, which matches that observed at -40 MPa 406

### 407 5. Conclusions

This work has presented a study of the thermal- and 408 409 stress-induced MT in [001] oriented Ni<sub>48 4</sub>Mn<sub>27</sub>Ga<sub>24 6</sub> single crystals. The thermal-induced transformation path is 410 austenite(A)  $\rightleftharpoons$  pre-martensite(PM)  $\rightleftharpoons$  10*M*. 411 Under stress, however, the 10M structure is stress-induced from 412 the PM via an intermediate MT, and thus, the inter-mar-413 tensitic transformation path is  $A \rightleftharpoons PM \rightleftharpoons I \rightleftharpoons 10M$ . 414 The I-phase is a modulated phase with a period between 415 that of the three-layer PM phase and the five-layer 10M416 phase based on previous investigations. From a compre-417 hensive study, including in situ DIC measurements of the 418 meso-scale full-field transformation strains during thermal 419 cycling under load, i.e., strain-temperature response, and 420 during isothermal load cycling, i.e., stress-strain, the fol-421 lowing conclusions are made: 422

1. The stress-free thermal-induced  $A \rightleftharpoons PM$  transforma-423 424 tion is localized. This is not immediately evident based on DSC analysis, in which two separate peaks exist, 425 which can imply  $A \rightleftharpoons PM$  and a subsequent  $PM \rightleftharpoons$ 426 10M inter-martensitic transformation. From in situ 427 DIC during thermal cycling under low constant com-428 pressive stress demonstrates, the transformation is more 429 likely  $A \rightleftharpoons A + PM$ , with austenite being the predomi-430 nant structure, followed by  $A + PM \Rightarrow 10M$ . From 431 432 in situ DIC during thermal cycling under constant compressive stress, we ascertain that a finite volume fraction 433 of austenite remains untransformed below  $M_{\rm f}$  for the 434 435 first DSC peak. This demonstrates that the initial transformation is more likely  $A \rightleftharpoons A + PM$ . 436

437 2. The transformation path at low constant stress levels is 438 primarily  $A \Rightarrow 10M$ . At higher levels of constant stress, 439 the path changes; two stages exist in the strain-temper-440 ature response. Based on findings from DIC analysis, 441 the initial stage corresponds to  $A \Rightarrow PM \Rightarrow I$  and the 442  $I \Rightarrow 10M$  inter-martensitic transformation takes place 443 throughout the second stage.

- 3. The inter-martensitic transformation  $A \rightleftharpoons PM \rightleftharpoons I$ 444 enhances elastic strain energy storage and curtails 445 energy dissipation in the strain-temperature response. 446 transformation Consequently, the path 447  $A \rightleftharpoons PM \rightleftharpoons I \rightleftharpoons 10M$  exhibits a smaller thermal hys-448 teresis compared with that for the predominantly 449  $A \rightleftharpoons 10M$  MT. 450
- 4. For the stress-strain response, two stages develop. In<br/>situ DIC analysis reveals that the first and second stages<br/>correspond to reorientation and de-twinning of PM and<br/>a subsequent  $PM \rightleftharpoons I \rightleftharpoons 10M$  inter-martensitic<br/>454<br/>transformation.451<br/>452
- 5. The inter-martensitic transition  $A \Rightarrow I \Rightarrow 10M$  takes place up to the highest compressive transformation stress levels. The transformation path is unequivocally confirmed from the in situ DIC strain fields, as the stress-strain response exhibits a single stage. 460
- 6. The PM, stress-induced I-phase and 10M martensite exhibit maximum strains of -0.75%, -2% and -4%, respectively.

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