Functional Stability of a Ferromagnetic Polycrystalline Ni$_2$MnGa High Temperature Shape Memory Alloy

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Abstract

Electrocaloric Ni$_2$MnGa is of interest for solid state refrigeration applications, as well as a high temperature thermal shape memory alloy. Here, polycrystalline Ni$_{42}$Mn$_{25}$Ga$_{33}$ is examined using in situ synchrotron X-ray diffraction. The initial martensite ($M_f$) and austenite ($A_f$) finish temperatures were found to be 232 °C and 298 °C respectively. $M_f$ was observed to decline by 8 °C/cycle and $A_f$ increased by 1 °C/cycle. Both below and surprisingly, above the Curie temperature, the application of an e.m.f. was found to affect the lattice parameters measured. A change in the thermal expansion of the two phases was found around the Curie temperature.

Keywords: Ferromagnetic shape memory alloy; synchrotron radiation; thermal expansion; intermetallic compounds

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Irrespective of composition, the austenite in Ni-Mn-Ga alloys is reported to be Fm$ar{3}$m but the martensite crystal structure varies with small changes in composition [15, 21]. Both modulated and non-modulated martensites have been reported; 5M and 7M martensites are observed in alloys with Curie temperatures ($T_c$) higher than $T_m$ whilst non-modulated martensites are observed in alloys where $T_c < T_m$ [15]. In Mn-rich alloys with ~20 at.% Ga, orthorhombic and tetragonal martensites are observed, and for certain compositions both forms can co-exist [21]. In the tetragonal martensite increase in $e/a$ increases the tetragonality, $c/a$ [19].

Single crystals have been used in most investigations of Ni-Mn-Ga alloys, but single crystal fabrication will limit the range of product forms that can be economically produced, so polycrystalline Ni-Mn-Ga alloys are highly desirable. In this context, purely thermal high temperature Ni$_2$MnGa actuators are also of interest, as conventional NiTi-based SMAs are limited to austenite finish temperatures of ~90°C. Normally, SMAs show significant functional fatigue, with the transformation temperatures dropping with each cycle, and so practical actuators with service lives of thousands of cycles remain difficult to produce.

Here, we focus on the characterisation of the thermal transformation in polycrystalline off-stoichiometry Ni$_{54}$Mn$_{25}$Ga$_{21}$ by synchrotron X-ray diffraction, with an emphasis on the evolution of the unit cell parameters of the phases. This particular composition was chosen to satisfy the requirement that the transformation be single step (cubic↔tetragonal) [22, 23] and to obtain a high temperature shape memory candidate with $T_m$ in excess of 200°C [22].

The alloy was prepared by vacuum arc melting pure elemental Ni, Mn and Ga in pure argon. The ingot was remelted four
times and inter-melt flipped to minimise elemental segregation.\textsuperscript{12,107} The \(\approx 60\) g ingot was encapsulated in a quartz tube and then\textsuperscript{108} homogenised at 900°C for 24 h. The ingot was then packed\textsuperscript{109} in Ti powder in a mild steel can and 80% hot rolled at 900°C.\textsuperscript{120} 0.5 \(\times\) 0.5 \(\times\) 30 mm gauge length specimens were then fabric\textsuperscript{121} cated by grinding and electro-discharge machining.\textsuperscript{122} Different\textsuperscript{123} straing calorimetry using a Mettler Toledo DSC 822\textsuperscript{e} in\textsuperscript{123} strument was used to obtain initial estimates of the transformation\textsuperscript{124} temperatures. The composition was also checked at this stage by SEM-EDX and found to be within the measurement\textsuperscript{126} error (\(\sim\) 0.5 at.\% of the target composition). Light element\textsuperscript{127} pickup such as O was therefore not determined. The specimens\textsuperscript{128} were then thermally cycled at a rate of 2 °C/s\textsuperscript{129} at zero load\textsuperscript{130} in an Instron5 kN resistance heating electro-thermal mechan\textsuperscript{130} ical testing machine (ETMT) at the ID15B powder diffraction\textsuperscript{131} beamline at the ESRF, Grenoble France, Figure 1. The same\textsuperscript{132} temperature was measured by using R-type thermocouples\textsuperscript{133} mounted on the sample surface, within 0.1 mm of the scanned\textsuperscript{134} volume. A wavelength of 0.1427 Å was used and the incident\textsuperscript{135} beam was approx. 0.5 \(\times\) 0.5 mm in size, giving a sampled vol\textsuperscript{136} ume of 0.5 \(\times\) 0.5 \(\times\) 0.5 = 0.125 mm\textsuperscript{3}. A Thales Pixium 4700\textsuperscript{37} detector [24] was used to collect complete Debye-Scherrer\textsuperscript{38} diffraction rings (Figure 1b) at a sample-detector distance of 1.228 m. A LaB\textsubscript{6} calibration powder was used to determine\textsuperscript{40} the instrument parameters. Phase fractions and lattice parameters were evaluated using the generalized structural analysis\textsuperscript{42} package (GSAS)\textsuperscript{[26, 27]} and the area detector analysis pack-\textsuperscript{43} age Fit2D [28]. Whole-ring integrations were used: the analysis\textsuperscript{44} was not found to be sensitive to orientation around the ring; e.g.\textsuperscript{45} there were no effects induced by, e.g. the rolling texture. This\textsuperscript{46} issue has been examined in our previous work [29, 30].\textsuperscript{47} The high temperature (austenite) phase in Ni\textsubscript{53}Mn\textsubscript{25}Ga\textsubscript{22} has\textsuperscript{48} an F m\textsubscript{3} crystal structure with Ni at (1/4, 1/4, 1/4), Mn\textsuperscript{49} at (1/2,1/2,1/2) and Ga at (0,0,0) and a\textsubscript{c} = 5.8468 \(\pm\) 0.0003 at 320 °C. For thermal cycling in the absence of stress and\textsuperscript{50} magnetic field, the martensite is tetragonal. The room tem\textsuperscript{51} perature lattice parameters of the martensite were found to be\textsuperscript{52} a\textsubscript{t} = 3.8391 \(\pm\) 0.0003, c\textsubscript{t} = 6.650 \(\pm\) 0.0001 and c\textsubscript{t}/a\textsubscript{t} = 1.732.\textsuperscript{53} Comparing these with the lattice parameters for Ni\textsubscript{53}Mn\textsubscript{25}Ga\textsubscript{22}\textsuperscript{54} reported by Cong et. al. [23] of a\textsubscript{c} = 3.865, c\textsubscript{c} = 6.596\textsuperscript{55} and c\textsubscript{c}/a\textsubscript{c} = 1.707, the increase in c/a ratio achieved by increasing Ni (at the expense of Ga) in the current alloy appears to\textsuperscript{56} change the c/a ratio considerably. The main orientation relationship in Ni\textsubscript{53}Mn\textsubscript{25}Ga\textsubscript{22} is reported to be (111)\parallel[101])\parallel[110],\parallel[111])\parallel[1, 31].\textsuperscript{57} The transformation sequence in the first thermal cycle is\textsuperscript{58} shown in Figure 2. A large dilation in the d\textsubscript{200} peak during the initial stages of cooling, but apart from\textsuperscript{59} this no additional peaks were observed elsewhere in the spectra.\textsuperscript{60} Therefore it is difficult to confirm the existence of an intermediate martensite phase. A subtle yet visible shift in the (200)\textsuperscript{61} tetragonal peak is observed (arrowed) on final cooling and before reheating began.\textsuperscript{62} The Rietveld-refined lattice parameters and phase fractions are\textsuperscript{63} shown in Figure 3. The transformation from tetragonal to cubic begins on heating at around 213°C with 80% of the cubic\textsuperscript{64} phase appearing over a temperature range of 227–258 °C,\textsuperscript{65} after which the transformation rate decreases with temperature be\textsuperscript{66} fore final completion at 286°C. The measurement points occur\textsuperscript{67} approximately every 5 °C, allowing the austenite and martensite\textsuperscript{68} start and finish temperatures (at 90% / 10% phase fraction) to\textsuperscript{69} be interpolated with an accuracy of around 3°C, Table 1. The fitted lattice parameters, Figure 3, show almost no shift between\textsuperscript{70} successive thermal cycles, which is a good indicator of thermal\textsuperscript{71} stability. For example, the change in a\textsubscript{t} at 125 °C after four\textsuperscript{72} thermal cycles was only 0.04% (Table 1). On initial heating, a\textsubscript{t}\textsuperscript{73} increased at a rate of \(\approx 77 \times 10^{-6} \text{ °C}^{-1}\) and c\textsubscript{t}\textsuperscript{74} decreases with a thermal expansion coefficient of \(\approx 69 \times 10^{-6} \text{ °C}^{-1}\). At \(\approx 160°C\)\textsuperscript{75} (near the Curie temperature estimated elsewhere [15, 23]), a visible change in linearity is observed and the thermal expansion / contraction appears to accelerate; i.e. a\textsubscript{t} then dilates and c\textsubscript{t} contracts at a more rapidly than before. These events are\textsuperscript{76} schematically highlighted in the final subtfigure in Figure 3. The reverse behaviour is observed on cooling and again the inflection\textsuperscript{77} point is \(\approx 160°C\). One can speculate that this change in\textsuperscript{78} thermal expansion is associated with a change in the magnetic\textsuperscript{79} ordering in the material in the vicinity of the reported Curie\textsuperscript{80} temperature; rationalisation of this result would benefit from in\textsuperscript{81} situ magnetic neutron diffraction measurements.\textsuperscript{82} In the cubic high temperature phase, the corresponding thermal\textsuperscript{83} expansion coefficient is measured to be \(13 \times 10^{-6} \text{ °C}^{-1}\).\textsuperscript{84} During transformation, contraction of c\textsubscript{t} initially ceases (at

Figure 1: (a) Schematic of the synchrotron X-ray diffraction setup, (b) Com-\textsuperscript{112} plete Debye-Scherrer rings from tetragonal martensite and (c) Diffraction spectra after 360° intensity integration across diffraction rings in (b)
Figure 2: Evolution of (sections of the) diffraction pattern during the first thermal cycle in Ni$_{54}$Mn$_{25}$Ga$_{21}$. The e.m.f reversal regime during which a shift in martensite lattice parameters was observed is indicated by arrows on the right.

≈ 235 °C, but during the final stages of transformation it resumes; a similar behaviour in reverse is observed for $a_t$. During cooling, at approximately 256 °C, indicated by arrow in Fig. 3, there appears to be a rather large instantaneous jump in both $c_t$ and the austenite lattice parameter. Remarkably, this phenomenon is only observed during cooling and in case of tetragonal martensite, it is only observed in the $c_t$ lattice parameter.

Interestingly, a hysteresis is observed in the lattice parameters in both the cubic and tetragonal phases, not associated with the transformation itself. In the first thermal cycle (brown / dark blue) which reversed at 345°C the lattice parameters converge at that point, whereas in subsequent cycles they converge at the end point of 300°C. This is a consequence of the resistance heating method used, where the direct current applied produces an e.m.f. which, in this ferromagnetic material, results in a change in the lattice parameters. However, the Curie temperature in these alloys is widely reported to be ≈110 °C [15]. This observation therefore poses a new question such as to whether these alloys shed their ferromagnetic properties completely, or not.

The lattice parameters are shown for the first, second and
fifth thermal cycle applied. It is notable that, whilst the lattice parameters at a given temperature are invariant with cycling, the transformation temperatures do evolve, by ~ 8 K/cycle for the austenite finish temperature $A_f$.

The evolution of the ETMT actuator position, along with the ex-situ DSC data, are shown in Figure 4. For comparison, DSC data for binary NiTi and two Ni$_{50}$Ti$_{15}$X$_{15}$ (X=Hf or Zr) high temperature shape memory alloys are also shown. The DSC results reproduce the observed transformation temperatures from the diffraction measurements and show a hysteresis ($A_t$-$M_t$) of around of 22 K in cycle 5. The austenite finish temperature gradually declines on cycling, but the martensite transformation temperatures remain constant, which is unusual compared to NiTi SMAs. In addition, the ETMT actuator position, which is in effect a dilatometry measurement over the entire sample length (some of which remained cold and did not transform), is shown. The transformation on heating results in a contraction of the sample which is reversed on cooling, but there is an evolution in the end-point actuator positions with cycling that indicates expansion of the sample from cycle 2 through 5. Since this occurs for the fcc austenite as well as the martensite, this cannot be due to the selection of preferred crystallographic variants and therefore must be due to the accumulation of plasticity, i.e. interface dislocations. By reference to conventional NiTi SMAs [32, 33], this would also be the reason for the gradual decline in the austenite transformation temperatures with cycling.

In summary, polycrystalline Ni$_{53}$Mn$_{25}$Ga$_{22}$ has been produced by a conventional ingot metallurgy and hot working approach. It is found to be a viable high temperature shape memory alloy material with $M_s = 236$ °C. The lattice parameters measured in both phases were found to be affected by the magnetic fields induced in the specimen by the applied ohmic heating method used, even above the expected Curie temperature of the alloy. Some functional fatigue was observed in the austenite transformation temperatures on heating. The thermal expansion / contraction of the tetragonal martensite $a_t$ and $c_t$ cell parameters were observed to accelerate above the expected Curie temperature.

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Table 1: Lattice parameters (Å) of tetragonal martensite on cooling and heating (at 125 °C for martensite and at 270 °C for austenite), where, c and h superscripts are for cooling and heating. $A_s$, $A_f$, $M_s$ and $M_f$ are austenite start, finish, martensite start and finish respectively.

<table>
<thead>
<tr>
<th></th>
<th>Cycle 1</th>
<th>Cycle 5</th>
</tr>
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<tbody>
<tr>
<td>$a^c_t$</td>
<td>3.8653 ± 0.0003</td>
<td>3.8667 ± 0.0004</td>
</tr>
<tr>
<td>$a^h_t$</td>
<td>3.8606 ± 0.0004</td>
<td>3.8604 ± 0.0003</td>
</tr>
<tr>
<td>$c^c_t$</td>
<td>6.603 ± 0.001</td>
<td>6.600 ± 0.001</td>
</tr>
<tr>
<td>$c^h_t$</td>
<td>6.611 ± 0.001</td>
<td>6.612 ± 0.001</td>
</tr>
<tr>
<td>$a^c_f$</td>
<td>5.8433 ± 0.0003</td>
<td>5.8425 ± 0.0002</td>
</tr>
<tr>
<td>$a^h_f$</td>
<td>5.8403 ± 0.0003</td>
<td>5.8403 ± 0.0002</td>
</tr>
</tbody>
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Austenite start, $A_s$ 226 227
Austenite finish, $A_f$ 298 258
Martensite start, $M_s$ 267 268
Martensite finish, $M_f$ 232 236

Figure 4: (a) Differential Scanning calorimeter (DSC) results obtained for five heating and five cooling cycles of as-rolled Ni$_{50}$Mn$_{25}$Ga$_{25}$ are shown, in comparison with the first cycle results for binary NiTi and as-rolled high temperature shape memory alloys Ni$_{50}$Ti$_{15}$Hf$_{15}$ and Ni$_{50}$Ti$_{15}$Zr$_{15}$ alloys and (b) Dilatation in macroscopic Ni$_{53}$Mn$_{25}$Ga$_{22}$ along the rolling direction during thermal cycling.

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