The thermal stability of high-temperature Ni–Mn–Ga alloys by ageing at temperatures in the range 620–770 K was studied. The results indicate that increasing the \( e/a \) ratio by substitution of Ga with Mn, keeping Ni close to stoichiometry, results in very stable alloys under ageing. However, increasing the \( e/a \) ratio by increasing the Ni content, either by substitution of Ga or reducing the Mn content, leads to faster decomposition.

Large magnetic field-induced strains observed in close to stoichiometric Ni\(_2\)MnGa alloys [1] have triggered interest in the so-called ferromagnetic shape memory alloys. In particular, the Ni–Mn–Ga system has been widely studied, aiming at the development of sensors and actuators based on magnetization changes as a function of the deformation or in the giant strains induced by a magnetic field, respectively. Ni–Mn–Ga alloys show a large temperature range where martensitic transformation (MT) can occur, and several alloys transforming at high-temperature were initially reported in 1995 [2]. More recently, other compositions of high-temperature Ni–Mn–Ga alloys have been studied [3–6], some of them showing good shape memory and superelastic properties [3,4]. However, commonly used shape memory alloys offer MT temperatures limited to \( \sim 400 \) K, and this fact has promoted interest in the research and development of high-temperature shape memory alloys (HTSMA) transforming above 400 K, as there are important possible fields for their application. Even though significant progress has been achieved using Cu-, Co-, NiTi-, NiAl- and Zr-based HTSMA, some of these still show drawbacks such as lack of stability or high brittleness [7–10]. Therefore, the study of Ni–Mn–Ga alloys as a new system in the field of HTSMA is a relatively unexplored but interesting topic, taking into account promising features such as high MT temperatures and good superelasticity.

The present work aims to characterize the MT evolution and microstructural changes produced by ageing at temperatures in the range 620–770 K in three polycrystalline Ni–Mn–Ga alloys. These compositions were chosen keeping, in each alloy, one element close to stoichiometric Ni\(_2\)MnGa, in order to check the thermal stability of the MT and ageing effects, both in martensite and in the parent phase, in a broad range of compositions.

Three polycrystalline alloys were prepared by induction melting in an argon atmosphere (from high purity elements, Ni 99.99\%, Mn 99\%, Ga 99.99\%), with nominal compositions: Ni\(_{58.3}\)Mn\(_{15.9}\)Ga\(_{25.8}\) (alloy 9), Ni\(_{51.2}\)Mn\(_{31.1}\)Ga\(_{17.7}\) (alloy 28) and Ni\(_{58.4}\)Mn\(_{25.3}\)Ga\(_{16.3}\) (alloy 29). After an initial treatment consisting of annealing at 1070 K followed by water quenching, the samples were aged in air at temperatures of 620, 670 and 770 K. The martensite start temperature \( (M_s) \) after the initial quenching was \( \sim 530 \) K for alloy 9, \( \sim 495 \) K for alloy 28 and \( \sim 470 \) K for alloy 29. After an initial treatment consisting of annealing at 1070 K followed by water quenching, the samples were aged in air at temperatures of 620, 670 and 770 K. The martensite start temperature \( (M_s) \) after the initial quenching was \( \sim 530 \) K for alloy 9, \( \sim 495 \) K for alloy 28 and \( \sim 470 \) K for alloy 29. The evolution of the MT characteristics was monitored by differential scanning calorimetry (DSC; Setaram 92 and Perkin–Elmer DSC-7) at selected times during the thermal treatment; after the DSC runs, ageing was resumed. Thermal cycling in the DSC was performed at 5 K min\(^{-1}\) and always kept in the range 360–670 K for alloy 9 and 300–620 K for alloy 28. Specific DSC cycles were carried out in alloy 29, which will be discussed below. Several
samples were subjected simultaneously to the same ageing series in order to check the possible effects of thermal cycling due to DSC runs and to prepare samples for microstructural analysis after relatively long ageing times. Samples for optical and transmission electron microscopy (TEM) were electrochemically polished in a solution of 20% (vol.) perchloric acid and 80% ethanol at room temperature (by double jet electropolishing at ~13 V and ~0.15 A for the TEM thin foils). TEM observations were performed in a Hitachi H600 at 100 kV, and at 200 kV in a Jeol-2011 high resolution electron microscope equipped with an energy dispersive X-ray (EDX) spectrometer.

Ageing series at 670 and 770 K were carried out in samples of alloy 9. The evolution of MT temperatures and transformation heat with ageing time, as obtained from the DSC runs, is shown in Figure 1. For the sake of clarity, only the forward \( T_f \) and reverse \( T_r \) transformation DSC peak temperatures are shown. The transformation heats plotted in Figure 1 correspond to the average for cooling and heating: \( Q = \frac{|Q_f| + |Q_r|}{2} \). Data corresponding to samples before ageing are plotted on the \( y \)-axis. It is worth noting an increase of ~30 K in the \( T_r \) values of the as-quenched samples of alloy 9, which is due to martensite stabilization. The MT is severely degraded after \( 2.1 \times 10^5 \) s (60 h) at 670 K; under ageing at 770 K, this time is shortened to \( 6 \times 10^5 \) s (17 h). Both \( T_f \) and \( T_r \) show parallel behaviour, even in their final drop, concomitant with the decrease in the heat exchanged \( Q \). An example of thermograms after different ageing times at 670 K is shown in Figure 2a–c.

Figure 1 also shows \( T_f \) and \( T_r \) values for a sample of alloy 28 aged at 770 K. No noticeable changes can be observed during the whole ageing process studied, either in the MT temperatures or in transformation heat \( (1.6 \times 10^7 \text{ s at } 770 \text{ K and } 1.9 \times 10^7 \text{ s, } \sim 216 \text{ days, at } 620 \text{ K).}

Alloy 29, with \( e/\alpha = 8.1 \), shows one of the highest MT temperatures reported in Ni–Mn–Ga alloys [2,6]. In this case, after water quenching from 1070 K, DSC heating runs performed at 5 K min \(^{-1}\) show a reverse transformation peak temperature \( T_r = 787 \text{ K, being necessary not to stop the run before 810–830 K in order to allow}

Figure 2. DSC cooling thermograms of alloy 9 after different ageing times at 670 K: (a) \( 10^5 \text{ s; (b) } 2.2 \times 10^5 \text{ s; (c) } 4.4 \times 10^5 \text{ s. First (d) and second (e) DSC heating runs at } 10 \text{ K min}^{-1} \text{ for as-quenched alloy 29.}

the sample to complete the retransformation. At these temperatures, fast degradation of the material takes place, even minimizing the time spent at temperatures above \( A_s \), which is clearly detected by a strong decrease in the heat exchanged in the next cooling cycle and in the subsequent runs. As it could be expected, heating the samples at higher rates (i.e., 20 K min \(^{-1}\) ) reduces the degradation of the alloy, but in any case it does not show an acceptable thermal stability when performing the reverse transformation. As an example, Figure 2d–e shows the mentioned degradation of the transformation after two consecutive thermograms up to 820 K at 10 K min \(^{-1}\). Occurrence of martensite stabilization was checked by keeping the samples at 670 and 720 K, just after the initial quenching treatment, for times up to 30 h. No distinctive features related to the stay at 670–720 K could be detected in the next DSC heating run, thus it must be concluded that the microstructural changes taking place during the reverse transformation override the martensite stabilization, if any. However, the thermal stability on ageing at 670 K up to \( 6 \times 10^7 \) s (7 days) appears to be very good according to the fact that the ageing does not modify the behaviour observed in the next retransformation, as commented above.

TEM observations were carried out in order to correlate the above-mentioned results with the eventual microstructural changes that developed in the samples after different stages of ageing. The microstructure of alloy 9 consists of big variants of non-modulated martensite (with a structure equivalent to a double L10), which are normally arranged in very fine internal twinning planes (up to a few nanometres wide) along \( \{111\}_{\text{L10}} \text{ planes (see inset in Fig. 3a). The small and irregular size of the twins is mainly responsible for the streaking along the } \{111\}_{\text{L10}} \text{ direction, which is perpendicular to the twinning planes in the image. No evidence of modulated martensites was detected in any of the three alloy samples studied. As-quenched samples of alloy 9 show practically total absence of precipitates, as well as a low concentration of dislocations whereas, after } 1.1 \times 10^5 \text{ s (30 h) ageing at } 670 \text{ K, a higher concentration of small precipitates and dislocations, often associated between them, can be observed. In some cases, the dislocations are grouped into bands, as shown in Figure 3a. Few lath-like precipitates have also been observed at this stage, although they are much more prominent after } 2.1 \times 10^5 \text{s.}

Figure 1. Evolution of DSC peak temperatures for the forward \( T_f \) and reverse \( T_r \) MT of alloy 9 aged at 670 K and alloy 28 aged at 770 K. The average transformation heat of alloy 9 aged at 670 K is also shown. Values on the \( y \)-axis correspond to the as-quenched samples.
(~57 h) of ageing at 670 K (Fig. 3b). Selected area electron diffraction patterns (SAEDP) obtained from these precipitates are normally identical to the ones of the L10 phase, except for those taken along the [111]_{L10} zone axis, which show extra spots, outlined by triangles in Figure 3b. Quantitative EDX measurements of these lath-like precipitates illustrate that the Ga content, which is the element closer to stoichiometric composition in this alloy, remains practically constant, whereas changes in Ni and Mn content bring about a final composition close to Ni3(Mn, Ga) (Table 1). Thus, as far as the morphology and composition are concerned, the process seems to be similar to the formation of Ni3Al lath-like precipitates in Ni–Al alloys [11,12]. However, despite these similarities, the SAEDP in Figure 3b cannot be described as the reported Ni3Al3 structure but as a supercell 3/2 times larger along the (112)_{L10}, than the original L10. Although more experiments need to be performed to clarify this point, the formation of this superstructure could be first attributed to an eventual ordering process of the Mn and Ga atoms that, obviously, cannot take place in the binary Ni–Ga or Ni–Al systems. Samples aged at 770 K show a different decomposition route from those aged at 670 K, leading to the formation of \(c_0\) phase. After \(6.2 \times 10^4\) s at 770 K, a few precipitates of this phase, with L12 structure, are already visible and, after \(6.2 \times 10^4\) s (17 h), in the last stage of the MT degradation, a dense distribution of precipitates can be clearly identified in several grains (Fig. 3c).

Table 1. Average EDX quantitative measurements for the precipitates (P), matrix (M) and inner precipitates (IP) obtained in the studied alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Zone</th>
<th>Ni (at. %)</th>
<th>Ga (at. %)</th>
<th>Mn (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 9 aged at 670 K</td>
<td>P</td>
<td>63</td>
<td>25</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>58</td>
<td>25</td>
<td>17</td>
</tr>
<tr>
<td>Alloy 9 aged at 770 K</td>
<td>P</td>
<td>70</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>58</td>
<td>25</td>
<td>17</td>
</tr>
<tr>
<td>Alloy 28 aged at 770 K</td>
<td>M</td>
<td>51</td>
<td>18</td>
<td>31</td>
</tr>
<tr>
<td>Alloy 29 before thermal</td>
<td>P</td>
<td>65</td>
<td>11</td>
<td>24</td>
</tr>
<tr>
<td>cycling in the DSC</td>
<td>IP</td>
<td>56</td>
<td>18</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>57</td>
<td>18</td>
<td>25</td>
</tr>
<tr>
<td>Alloy 29 after thermal</td>
<td>P</td>
<td>66</td>
<td>11</td>
<td>23</td>
</tr>
<tr>
<td>cycling in the DSC</td>
<td>IP</td>
<td>54</td>
<td>18</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>57</td>
<td>19</td>
<td>24</td>
</tr>
</tbody>
</table>

The microstructure of alloy 28 prior to any ageing treatment consists of big variants of non-modulated twinned martensite (L10) with almost a total absence of precipitates, similar to the microstructure of alloy 9. Few small precipitates and dislocations can be seen in alloy 28 aged for \(2.2 \times 10^6\) s (~620 h) at 770 K (Fig. 4a). After ageing at 770 K for \(1.6 \times 10^7\) s, no significant differences in the microstructure are apparent, indicating a high resistance of this alloy against
decomposition. In any case, the effect on the MT produced by such a small number of defects seems to be undetectable, as seen by the DSC runs.

The effect of thermal cycles carried out to follow the macroscopic evolution of the MT, as commented above, has been checked by subjecting several samples to equal ageing series, but without performing the intermediate DSC cycles in some of them. As an example, a sample of alloy 28, aged for 2.2 × 10^6 s at 770 K, does not show significant microstructural differences from another sample subjected to 20 DSC cycles before reaching the same ageing time. This result and similar behaviour found in alloy 9 could be expected, taking into account the good stability of the MT under thermal cycling between room temperature and 620 K reported for alloy Ni53Mn25Ga21 transforming at temperatures close to those of alloy 28 [14].

Relatively large precipitates, some of them with dendrite shape and over 10 μm long, can be seen in the as-quenched alloy 29 (Fig. 4b). They show a disordered fcc structure, therefore being commonly denoted as γ instead of γ’.

EDX microanalysis shows that these precipitates have a Mn content very similar to the matrix, being richer in Ni and poorer in Ga (Table 1). It is worth noting that, as in alloy 9, the element which is close to the stoichiometry is the one that keeps nearly the same content in the matrix and the precipitates. Apart from these precipitates, the matrix of alloy 29 is formed by variants of L10 non-modulated martensite, as in the previous cases. As mentioned above, two DSC runs up to A_f (810 K) performed at 5 K min^{-1} produce severe degradation of the transformation. Quantitative EDX measurements in these samples show an average chemical composition similar to the as-quenched ones (Table 1) but with a much higher dispersion of the data obtained in the matrix, pointing to a chemical decomposition of the parent phase. For instance, the standard deviations of the matrix composition detailed in Table 1, taking into account all the measurements performed under similar parameters, are <0.5 at.% for all cases except thermally cycled alloy 29, with values close to 2 at.%.

Although it seems clear that a chemical decomposition takes place, no signs of any massive precipitation were observed after these initial heating runs. Nevertheless, these runs promote the ordering of the precipitates from γ to γ’, keeping the same chemical composition (Fig. 4c). The quenching process retains the lower order of the γ precipitates, stable at 1070 K, which evolves to the γ’ structure when the temperature is high enough to allow atomic diffusion.

Considering the composition dependence of MT temperatures in the alloys studied, alloy 9 extrapolates relatively well the trends of Ni_{50+x}Mn_{25−x}Ga_{25} alloys for the transformation temperatures vs x or vs e/a shown in Ref. [15], as alloy 9 can be considered, with a good approximation, as an alloy with x ≈ 8.3 (e/a = 7.72). In a similar way, alloy 29 follows the behaviour of Ni_{50+x}Mn_{25}Ga_{25−x} also shown in [15,16] with y ≈ 8.4 (e/a = 8.1). Both alloys extend the domain of e/a values which follow approximately a linear relationship with the transformation temperatures, therefore ternary alloys far from stoichiometry can be designed with a good knowledge of their MT range.

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