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Thermal stability of high-temperature Ni–Mn–Ga alloys

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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.

Keywords: Ageing; Shape memory alloys; Martensitic phase transformation; Precipitation; Thermal stability

Large magnetic field-induced strains observed in close to stoichiometric Ni_2MnGa 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 ~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_2MnGa, 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 ~530 K for alloy 9, ~495 K for alloy 28 and ~740 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

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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: $Q = [|Q_f| + |Q_r|]/2$. 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 ~2.1×10^5 s (~60 h) at 670 K; under ageing at 770 K, this time is shortened to ~6×10^4 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_r and T_f 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 (1.6×10^7 s at 770 K and 1.9×10^7 s, ~216 days, at 620 K).

Alloy 29, with $e/a = 8.1$, 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 $T_r = 787$ K, being necessary not to stop the run before 810–830 K in order to allow

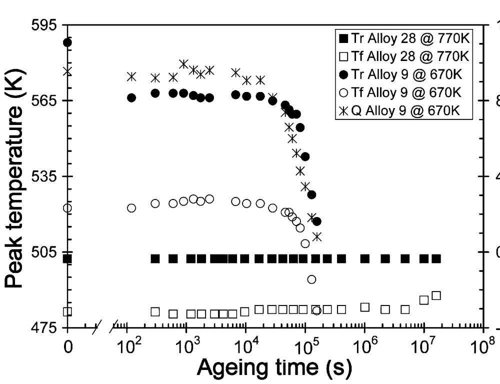

Figure 1. Evolution of DSC peak temperatures for the forward T_f and reverse T_r MT of alloy 9 aged at 670 K and alloy 28 aged at 770 K. The average transformation heat of alloy 9 aged at 670 K is also shown. Values on the y-axis correspond to the as-quenched samples.

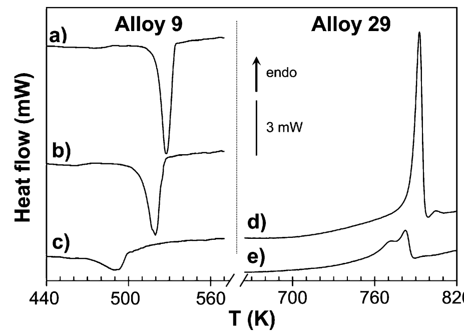

Figure 2. DSC cooling thermograms of alloy 9 after different ageing times at 670 K: (a) 10^3 s; (b) 2.2×10^4 s; (c) 4.4×10^4 s. First (d) and second (e) DSC heating runs at 10 K min^{-1} for as-quenched alloy 29.

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_f, 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 6×10^5 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 $L1_0$), which are normally arranged in very fine internal twins (up to a few nanometres wide) along $(1\bar{1}1)_{L1_0}$ planes (see inset in Fig. 3a). The small and irregular size of the twins is mainly responsible for the streaking along the $\langle 1\bar{1}1\rangle^*_{L1_0}$ 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 1.1×10^5 s (30 h) ageing at 670 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 2.1×10^5 s