Thermal stability and ordering effects in Ni–Fe–Ga ferromagnetic shape memory alloys

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Abstract

The martensitic transformation (MT) from L2\textsubscript{1} (Heusler) structure to layered martensites in three polycrystalline Ni\textsubscript{53.5+x}Fe\textsubscript{19.5−x}Ga\textsubscript{27.0} alloys, with \(x = 0, 0.5,\) and 1.5 at.%, has been monitored by differential scanning calorimetry and transmission electron microscopy in order to follow the evolution under ageing in parent phase as well as the effect of atomic order on the MT temperatures. Ageing at 670 and 770 K produces degradation of the MT after 10\textsuperscript{5}–10\textsuperscript{6} s, concomitant with the appearance of small (<1 \(\mu\)m), elongated \(\gamma\) particles. Water quenching from different temperatures (470–1070 K) causes an increase in MT temperatures compared to slow cooled samples. This effect is related to a decrease of the L2\textsubscript{1} order of the parent phase upon quenching, promoting an increase in the MT temperatures. The effect is maximum after quenching from 970 K; a temperature just above the B\textsubscript{2}–L2\textsubscript{1} order transition. As for the magnetic properties, order leads to larger saturation magnetization and higher Curie temperatures.

Keywords: Ferromagnetic shape memory alloys; Order degree; Thermal stability; Quenching; Magnetic properties (magnetization, Curie temperature)

1. Introduction

The brittleness of Ni\textsubscript{2}MnGa Heusler-type alloys is promoting the development of other ferromagnetic shape memory alloy (FSMA) systems, as for example Co–Ni–Ga \cite{1,2} and Ni–Fe–Ga \cite{3,4}. Near-stoichiometric Ni\textsubscript{2}FeGa alloys represent one of the better alternatives to Ni–Mn–Ga FSMA, as they undergo a martensitic transformation (MT) from L2\textsubscript{1} structure to ferromagnetic martensites with layered structures (i.e. five-layered, 10M; seven-layered, 14M \cite{3,4}), for which large magnetic-field-induced strains (MFIS) have been found in Ni–Mn–Ga alloys. Reported magnetocrystalline anisotropy values in Ni–Fe–Ga are close to those of Ni–Mn–Ga alloys, although the MFIS obtained up to date are much lower in Ni–Fe–Ga \cite{5}. Moreover, Ni–Fe–Ga alloy compositions can be selected in order to obtain a MT domain close to room temperature \cite{4}, which is an essential requirement for most possible applications. Another important issue is the possibility to tailor a dual phase microstructure by including small amounts of \(\gamma\) phase, through proper thermal treatments, which will increase the ductility of Ni–Fe–Ga alloys, thus opening a way to overcome the high brittleness of Ni–Mn–Ga.

Few results have been reported up to now on the influence of heat treatments (i.e. annealing and/or ageing at intermediate temperatures) on the MT of Ni–Fe–Ga alloys and its relation to the evolution of the \(\beta + \gamma\) microstructure \cite{6–9}. Another important point is to know the effect of the degree of order on the MT characteristics (transformation temperatures, transformation kinetics) \cite{10} and on the magnetic properties. In this work, some more results of parent phase ageing at moderate temperatures and atomic order effects on MT and magnetic properties are presented.

2. Experimental procedure

Three polycrystalline Ni\textsubscript{53.5+x}Fe\textsubscript{19.5−x}Ga\textsubscript{27.0} alloys, with \(x = 0, 0.5,\) and 1.5 at.%, named A, B, and C, respectively, were cast by induction melting in Ar. After a solution treatment of
2 h at 1270 K in Ar atmosphere followed by slow cooling, the alloys show martensite start temperatures, \( T_s \approx 255, 275, \) and 325 K for alloys A, B, and C, respectively. Ageing series in air at 520, 670, and 770 K for different times, followed by air cooling to room temperature, were carried out in samples spark-cut from the annealed ingots. Atomic order effects were checked either by quenching to water at room temperature or air cooling from temperatures in the range 470–1070 K. The holding times before quenching or air cooling were \( \sim 10^3 \) s. The evolution of the MT characteristics was monitored by differential scanning calorimetry (DSC). Samples for transmission electron microscopy (TEM) were electrochemically polished by double jet at \( \sim 16 \) V and \( \sim 0.22 \) A in a 20% perchloric +80% ethanol solution at room temperature. TEM observations were carried out in a Hitachi H600 (100 kV) and in a JEOL 2011 (200 kV) high-resolution electron microscope equipped with an energy-dispersive X-ray spectrometry (EDX) spectrometer. A Quantum Design MPMS XL-7 SQUID magnetometer [11] has been used to measure the temperature dependence of the dc magnetization under a 6 T applied field.

3. Results and discussion

The three alloys show very good thermal stability, that is practically no evolution in both transformation temperatures and heat exchanged, upon ageing at 520 K for time periods up to \( \sim 10^2 \) s. At higher ageing temperatures (670 and 770 K), considering the parallel evolution of forward and reverse MT temperatures with ageing time, the peak temperatures of DSC thermograms are representative of transformation temperatures behaviour. Fig. 1 compares the DSC peak temperatures of the reverse transformation (obtained as the average of two DSC runs) as a function of ageing time for alloy B and for the three ageing temperatures. Data corresponding to samples as-annealed have been added on the y-axis. It is worth to note, as commented above, only a slight increase (\( \approx 2–3 \) K) of MT temperatures occurs after \( 10^2 \) s at 520 K. Ageing at 670 and 770 K produces a degradation of the MT, visible as a decrease in transformation temperatures, for time periods between \( 10^2 \) and \( 10^3 \) s, obviously the shorter for the higher temperature. A parallel evolution is found in the latent heat of the MT, accompanied by a broadening of the DSC signals [9]. Results for alloy A after ageing at 670 and 770 K are fully equivalent to those presented for alloy B, whereas the alloy C, with lower Fe content (and higher MT temperatures), shows its degradation at shorter ageing times than alloys A and B, as it can be seen in Fig. 2. There is a slight but continuous decrease in the MT temperatures, and the calorimetric signal is almost completely lost after \( 10^3 \) s at 770 K in alloy C. The initial increase of MT temperatures for short ageing times with respect to the as-annealed samples, as can be seen in Figs. 1 and 2, is due to a relatively higher L21 order degree present in the samples before ageing, which is fully coherent with the ordering results shown below. TEM examinations after these short ageing times confirm the absence of any changes in the structure, microstructure and defects distribution with respect to the as-annealed samples. A similar effect on the MT temperatures of short ageing time has also been reported in other Ni–Fe–Ga alloys [6].

The microstructure before ageing is characterized by the presence of large \( \gamma \) phase precipitates, several micrometers in average, mostly located at the grain boundaries, in the alloys A and B. In the alloy C the \( \gamma \) phase is also found inside the grains, thus showing a higher amount of second phase than alloys A and B. Heterogeneous distributions of small (\( < 1 \mu m \)) and elongated \( \gamma \) precipitates inside the grains are found after ageing periods within the plateaus seen in Figs. 1 and 2 (that is, for ageing times below \( \sim 10^6 \) s at 670 K or \( \sim 10^5 \) s at 770 K, for alloys A and B, about one order of magnitude lower for alloy C). Some groups of few precipitates of micron sizes can also be found. For ageing times larger than those mentioned above, leading to the degradation of the MT (and concomitant decrease in the transformation temperatures), agglomerations of large \( \gamma \) phase precipitates are formed (Fig. 3). EDX analysis of these precipitates confirm that they are richer in Fe and poorer in Ga, compared to the matrix. Thus, Ga and Fe changes in the matrix, induced by the precipitation, tend to reduce the \( el/a \) ratio and correspondingly the MT temperatures in agreement with its \( el/a \) dependence [12]. The three alloys transform to a mixture of five-layered (10M), six-layered (6M) and seven-layered (14M) martensites.

In order to check the effects of atomic order on the MT, samples were subjected to quenching treatments from different temperatures (treatment TT1), afterwards to slow cooling treatments from the same temperatures (TT2) and finally again to quench treatments as in TT1 (TT3). Fig. 4 shows the DSC peak temperatures obtained in the first reverse and next direct
MT of alloy C after the different thermal treatments. The peak temperatures increase as quenching temperature increases from 470 to 970 K. For the TT1 treatment at 1070 K, the peak drops again at levels similar to those of TT1 at 670 K. MT temperatures of the samples slowly cooled do not show any significant dependence on the treatment temperature, being close to those of solution treated samples. TT3 treatments produce very similar effects than TT1, therefore confirming that no permanent effects are induced after these treatments. It is worth to note the similarity of the shifts in the temperatures of the direct and reverse MT produced by quenching, with respect to slowly cooled samples, as shown in Fig. 4. These features occur also for alloys A and B in a fully equivalent way [10]. It should be noted that the MT range of as-annealed alloy C is slightly above room temperature, thus all the treatments performed in alloy C samples ended in martensite phase. The same happens to samples of alloys A and B after some quenching treatments. Therefore, it could be considered that martensite stabilization is the mechanism responsible for the MT shifts after the different thermal treatments. However, as the subsequent direct transformations, after a first complete reverse MT, also show the same shifts in the transformation temperatures, martensite stabilization has to be discarded. The increase in MT temperatures after TT1 and TT3 treatments has to be ascribed to the decrease in the degree of L21 order retained after quenching, with respect to the as-annealed or slowly cooled samples. Taking into account that the L21 → B2 transition has a peak at about 930 K, as seen by DSC [10], it is worth to explain the maximum shift in MT range (and maximum degree of retained L21 disorder) for quenching temperatures of 970 K, as well as a minor shift when quenching temperatures are higher (i.e. 1070 K), considering the higher vacancy concentration in this case, which promotes a more efficient vacancy assisted diffusion and a higher order degree. The shifts observed in a Ni$_3$Fe$_{20}$Ga$_{27}$ alloy after annealing at different temperatures followed by quenching [6] can be understood as due to retained disorder upon quench. Quenching effects are visible not only through the MT temperatures but also in the kinetics of the transformation. As temperatures for TT1 or TT3 treatments increase up to 970 K, the jerkiness of the direct transformation increases,
leading to a very broad and jerky transformation after quench from 970 K, in strong contrast with the slow cooled samples.

Finally, the influence of the order degree on the magnetic behavior has been analyzed through the temperature dependence of magnetization, $M$ (applied magnetic field, $\mu_0 H = 6 \, \text{T}$) in alloy A. Fig. 5 shows the temperature evolution of $M$ for the different thermal treatments. The martensitic transformation can be observed as a step in the magnetization curve. The inset in Fig. 5 shows the evolution of the martensite start and Curie temperatures ($T_S$ and $T_C$, respectively) for the different thermal treatments. Increasing the quenching temperature increases the temperature of the MT in agreement with the results shown above. The Curie temperature of the alloy decreases with the quenching temperatures as a consequence of the decrease in the order degree of the alloy.

In order to better understand the magnetization process, the low temperature magnetization curve has been analyzed by the Block approximation $M = M_S(0)(1 - \beta T^{3/2})$ [13], where $M_S(0)$ is the saturation magnetization at 0 K and $\beta$ is the characteristic constant of spin-wave excitations. Fig. 6 shows the evolution of the saturation magnetization $M_S$ and the $\beta$ parameter for the different quenching temperatures. An increase in the quenching temperature gives rise to a decrease in $M_S$ and an increase in $\beta$. Then, the atomic order promotes an increase in magnetization of the alloy and a decrease in the $\beta$ parameter as a consequence of the enhancement in the exchange interaction. The reduction in the order parameter decreases the exchange integral (evidenced by the reduction in the saturation magnetization) and, as a consequence, induces an increase in the $\beta$ parameter.

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**References**