Effect of precipitates on the stress–strain behavior under compression in polycrystalline Ni–Fe–Ga alloys

F. Masdeu, J. Pons, R. Santamarta, E. Cesari, J. Dutkiewicz

Abstract

The stress–strain behavior under compression has been studied in three Ni$_{55-x}$Fe$_{18+x}$Ga$_{27}$ ($x = 0, 1, 1.5$ at.%) polycrystalline alloys with different distributions of γ phase precipitates. All the alloys present the superelastic effect at temperatures above the austenite-finish temperature and the mechanical tests confirm the linear dependence of the critical stress with temperature, as described by Clausius–Clapeyron-type equation. The ‘plateau’ in the stress–strain curves, associated to the stress-induced transformation, presents an increasing slope as samples contain a higher amount of inter-granular particles. This hardening effect is due to the enhanced difficulty to accommodate the deformation between adjacent grains. Intra-granular precipitates increase still further the hardening effect, as a consequence of the difficulties found by the growing martensitic plates to overcome the precipitates. Furthermore, the maximum observed stress-induced strain is notably reduced in samples containing higher fractions of γ precipitates. These precipitates also have an effect in the deformation of martensite, increasing the stress needed to rearrange the variants.

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1. Introduction

The large magnetic field-induced strain obtained in near to stoichiometric Ni$_2$MnGa [1] has triggered the interest in ferromagnetic shape memory alloys (FSMA) and is promoting the development of other FSMA systems such as Ni–Fe–Ga, Co–Ni–Ga, etc.

It is well known that brittleness is one of the main problems in most of the ferromagnetic shape memory alloys. Some studies on Co–Ni–Al and Ni–Al polycrystalline shape memory alloys [2,3] reported that the high brittleness of the alloy decreases by the presence of second phase precipitates, which can be introduced into the β phase by choosing proper compositions and thermal treatments [4]. Some works on mechanical properties of Ni–Fe–Ga shape memory alloys have been carried out, but mostly in single crystals [5,6]. In this work, the effect of content and location of γ phase precipitates on the stress–strain behavior under compression of three Ni–Fe–Ga polycrystalline alloys has been studied. Depending on the alloy composition and heat treatment, the distribution of precipitates will be different, modifying the mechanical properties of the alloy. The tests were carried out on specimens free of γ phase, specimens containing intergranular precipitates and in specimens containing inter and intragranular precipitates. As expected, alloys containing intergranular precipitates are able to resist higher stresses before fracture.

2. Experimental procedure

Three polycrystalline alloys of nominal composition Ni$_{55-x}$Fe$_{18+x}$Ga$_{27}$ ($x = 0, 1, 1.5$ at.%.) were produced by induction melting followed by slow cooling in two casting series. After casting, the first set of alloys was subsequently annealed for 2 h at 1270 K in argon flow. This treatment will be denoted as T2. For the second set of alloys produced, one portion was kept in the as-cast condition (T0) and the other portion was annealed for 6 h at 1270 K, also in argon flow (T6). The heat treatments T2 and T6 were also followed by slow cooling.

The nominal composition of the alloys and the martensitic transformation temperatures (MTT), martensite-start temper-
Table 1 Composition, in at.%, and $M_s$ and $A_f$ temperatures, in K, of the tested alloys

<table>
<thead>
<tr>
<th>Comp. (at.%)</th>
<th>53.5Ni–19.5Fe–27.0Ga</th>
<th>54.0Ni–19.0Fe–27.0Ga</th>
<th>55.0Ni–18.0Fe–27.0G a</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-T0</td>
<td>251</td>
<td>278</td>
<td>324</td>
</tr>
<tr>
<td>A-T2</td>
<td>256</td>
<td>277</td>
<td>327</td>
</tr>
<tr>
<td>A-T6</td>
<td>253</td>
<td>274</td>
<td>326</td>
</tr>
<tr>
<td>B-T0</td>
<td>283</td>
<td>282</td>
<td>330</td>
</tr>
<tr>
<td>B-T2</td>
<td>282</td>
<td>281</td>
<td>335</td>
</tr>
<tr>
<td>B-T6</td>
<td>281</td>
<td>324</td>
<td>332</td>
</tr>
<tr>
<td>C-T0</td>
<td>330</td>
<td>335</td>
<td>335</td>
</tr>
<tr>
<td>C-T2</td>
<td>335</td>
<td>335</td>
<td>335</td>
</tr>
<tr>
<td>C-T6</td>
<td>335</td>
<td>335</td>
<td>335</td>
</tr>
</tbody>
</table>

$M_s$ and austenite finish temperature $A_f$, measured by differential scanning calorimetry (DSC), are shown in Table 1.

Specimens of $\sim 3 \text{ mm} \times 3 \text{ mm} \times 9 \text{ mm}$ for compression tests were obtained by spark-cutting. The tests were carried out using a Zwick Z100 mechanical testing machine (cross-head speed 0.1 mm/min) in a range of temperatures from room temperature (291 K) to 373 K for alloys A and B, and to 403 K for alloy C, in steps of 10 K. Thus, the alloys A and B were tested at temperatures above $A_f$ (i.e. in austenitic state) and alloy C at temperatures between $M_f$ and $A_f$ and above $A_f$. Specimens were heated at 470 K for 3 min after each mechanical test in order to retransform any eventually retained martensite.

3. Results and discussion

The microstructure of the different samples depends on the composition and on the heat treatment. The as-cast alloys of the second series (treatment T0) were completely free of $\gamma$ phase particles, while the annealed specimens presented different distributions of $\gamma$ precipitates (Fig. 1). Samples A-T2/T6 and B-T2/T6 show particles of $\gamma$ phase located only at the grain boundaries (Fig. 1). The amount of inter-granular precipitates is slightly higher in the annealed samples of alloys A than in alloys B. The samples C contain, in addition, intragranular precipitates, with a low (T6) and high (T2) content (see Fig. 1). The specimens were cut from a cylindrical ingot formed by grains about 250 $\mu$m in diameter.

The MTT do not present big changes with the applied heat treatments (see Table 1). As all the heat treatments were followed by slow cooling, the atomic ordering, which is known to affect the MTT [7], is approximately the same in all cases. Thus, the presence of precipitates does not strongly affect the MTT. However, the DSC peaks become wider in alloys containing $\gamma$ phase.

The specimens free of $\gamma$ phase (alloys A, B and C after the T0 thermal treatment) show a high brittleness. In these specimens the cracks start to propagate during the first mechanical test, and after 4–5 cycles the specimens collapse by intergranular fracture. The maximum stress resisted by these samples is around 250 MPa for any of the three compositions. The whole stress-induced strain can reach 3.5–4%, showing a total recovery upon unloading. The alloys containing intergranular precipitates are able to resist around 500 MPa and larger number of mechanical cycles (about 50) without cracking. Therefore, intergranular precipitates improve the cohesion between grains, thus increasing the ductility of the material.

Fig. 2 shows some stress–strain curves registered in samples A-T2 at different temperatures above $A_f$, so starting from austenite L21. The superelastic effect takes place in all the studied range of temperatures. The curves show a single transformation step, reaching deformations associated to the transformation slightly higher than 2% at room temperature. As expected from their similar microstructures, the stress–strain behavior of the other annealed samples of alloys A and B is very similar to that shown in Fig. 2. It is worth noting, in Fig. 2 and other figures showing $\sigma$-$\varepsilon$ curves, a non-linear part at the lowest stresses, corresponding to the initial deformation of austenite, due to the accommodation between grips and specimen.

The hardening of austenite as the temperature increases leads to an increasing difficulty in accommodating the martensitic phase, therefore increasing stresses are needed to achieve similar
transformation degrees, visible as the hardening in the transformation ‘plateau’. Although the total deformation reached in the registered curves is nearly the same at different temperatures, the transformed fraction is lower at higher temperatures, this fact being responsible for the reduction in the hysteresis observed in these cases.

Fig. 3 presents some of the stress–strain curves registered in C-T6 specimens. The tests carried out at room temperature (291 K) correspond to the rearrangement of the martensite variants, leading to a remaining strain of 2.4%. Even at 333 K, close to $A_f$, a residual strain is observed after unloading. At higher temperatures, the superelastic effect is observed, although the deformation associated to the martensitic transformation is slightly lower than in the annealed samples of alloys A and B, due to the higher content of intergranular $\gamma$ phase.

The stress–strain curves of C-T2 samples, containing also intra-granular precipitates are shown in Fig. 4. The curve registered at 291 K, below $M_f$, corresponds to rearrangement of the preexisting variants of martensite, leading to a permanent strain of 2% after unloading. Above 333K, the superelastic effect is again observed. The smaller strain obtained in alloy C-T2, as compared to previous cases, is due to the presence of additional intragranular $\gamma$ precipitates. Taking into account the larger fraction of $\gamma$ phase and that the surrounding regions do not transform into martensite within the normal range as revealed by scanning electron microscopy (SEM) (Fig. 5), the volume fraction transforming to martensite decreases significantly. Energy-dispersive X-ray spectrometry microanalysis shows that the surrounding regions (in austenitic phase) become poorer in Fe and richer in Ga. In this way, the $e/a$ ratio decrease in these regions, thus decreasing the MTT.

Fig. 2. Compression stress–strain curves registered at different temperatures of the A-T2 alloy.

Fig. 3. Compression stress–strain curves of the C-T6 alloy registered at different temperatures.

Fig. 4. Evolution of stress–strain behavior with temperature for C-T2 alloy.

Fig. 5. SEM image of an intragranular precipitate obtained at room temperature, showing the surrounding matrix still in parent phase.

Fig. 6. Comparison of stress–strain curves of specimens showing different distribution of $\gamma$ phase precipitates.
Fig. 6 shows stress–strain curves for different alloys and treatments registered at equivalent distance in temperature from $M_c$. The plot allows to compare the effect of $\gamma$ phase precipitates, according to their content and location. Alloy A-T0 (free of $\gamma$ phase) exhibits a large ‘plateau’ associated to the martensitic transformation. The samples containing $\gamma$ precipitates show a hardening effect during the transformation, revealed by an increase in the slope of the transformation ‘plateau’. As mentioned above, alloys A-T2 and B-T6 show a very similar behavior, although the content of $\gamma$ phase is slightly higher in B-T6. Elastic modulus, as well as transformation strain and hardening exhibited in the ‘plateau’ are roughly identical. For higher content of intergranular precipitates (C-T6), the transformation strain becomes lower and the hardening effect increases, due to the enhanced difficulty to accommodate the deformation associated to the martensitic transformation between adjacent grains. Alloys containing intragranular precipitates (C-T2) show a very strong hardening during the transformation and variant reorientation as well as a lower strain. This is due to the difficulties of the martensite plates to overcome the intragranular precipitates and their untransformed surrounding areas, as revealed by the fact that the martensite plates observed by optical microscopy after the temperature induced transformation are narrower compared than those formed in alloys free of intragranular precipitates. In stress induced transformations, the inhomogeneous stress fields around the precipitates could also promote the formation of variants different than those selected by the applied stress, further reducing in this way the macroscopic strain achieved. Fig. 6 also reveals that the elastic modulus, at temperatures equally shifted from the corresponding $M_c$, is very similar for all three alloys containing only intergranular precipitates, but intragranular precipitates (sample C-T2) contribute to increase the elastic modulus of the material.

The tests carried out at different temperatures confirm the linear dependence of critical stress to induce the transformation with temperature (Fig. 7). The critical stress values were determined as the crossing of tangents to the elastic loading of austenite and to the transformation ‘plateau’. Experimental Clausius–Clapeyron constants ($d\sigma_c/dT$) are approximately the same for all three alloys: 2.4 MPa/K for A-T2, 2.1 MPa/K for B-T2/T6, 2.3 MPa/K for C-T2 and 2.1 MPa/K for C-T6. These values are slightly lower than those obtained in single crystals for Ni$_5$Ga$_{27}$Fe$_{19}$ alloy under compression [5], which are around 3 MPa/K for [1 2 3] and [0 1 1] directions.

4. Conclusions

The effect of $\gamma$ phase precipitates on the stress–strain behavior of Ni–Fe–Ga alloys has been studied. Specimens free of precipitates, or with a very low content, show a high brittleness, due to the poor cohesion between adjacent grains. The presence of $\gamma$ phase precipitates plays a different role depending on their location: inter or intragranular. Intragranular precipitates improve the cohesion between grains, thus increasing the ductility of the alloy. As the $\gamma$ phase content increases, the strain related to the transformation decreases and the hardening associated to the ‘plateau’ becomes higher.

Intragranular $\gamma$ phase precipitates further reduce the volume fraction of austenite able to transform into martensite. The $\gamma$ phase precipitates inside the grains bring about smaller martensite plates, as needed for the elastic accommodation of the inhomogeneous stress fields around the particles. This fact, and the observation of untransformable regions around the precipitates (due to changes in composition) make the macroscopic deformation associated to the transformation to decrease. Intragranular precipitates also increase the elastic modulus of austenite and the hardening effect during the martensitic transformation or variant reorientation.

All the studied specimens present a linear dependence of critical stress with temperature, the Clausius–Clapeyron constants being very similar (considering their uncertainty) for the different distributions of precipitates.

Acknowledgements

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References