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Effect of oriented γ' precipitates on shape memory effect and superelasticity in Co–Ni–Ga single crystals

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Abstract

This paper reports on the effect of dense dispersions of nanometric γ' precipitates on the shape memory and superelastic response of $Co_{49}Ni_{21}Ga_{30}$ single crystals. The particles are grown by ageing at 620 K with or without applied stress, which leads to oriented single-variant or non-oriented four-variant precipitates with a habit plane on one or four $\langle 1\,1\,1\rangle_{B2}$-type planes, respectively. The non-oriented precipitates strongly decrease the martensitic transformation temperatures, enhance the transformation hysteresis and decrease the recoverable strain. These effects are significantly reduced in the case of oriented particles. The effects are correlated with difficulties in accommodating the $L1_0$ martensite within the irregular stress fields generated by the non-oriented precipitates, which cause a micromodulation of the martensitic structure. In turn, the collective effect of the stress fields around the oriented precipitates improves the martensite accommodation, which is reflected in higher transformation temperatures, lower hysteresis, larger transformation strain and smoother σ–ε curves during the stress-induced transformation plateau, in comparison to non-oriented particles. The samples containing nanometric γ' particles present several stages in the (σ, T) diagram and lower values of the slope $d\sigma/dT$, compared to the precipitate-free material. This fact has been related to the temperature dependencies of the irreversible dissipation energy and transformation strain. The nanometric precipitates strengthen the B2 matrix and enlarge the temperature range for superelasticity above 570 K. In addition, the particles difficult the detwinning process of the stress-induced martensite, which produces microplastic deformation by slip and tiny martensite plates are retained around the particles after the mechanical tests.

Keywords: Shape memory alloys (SMAs); Nanoparticles; Two-phase materials; High-resolution electron microscopy; Mechanical testing

1. Introduction

In the last decade or so, research has focused on the search for materials showing high-temperature shape memory effect (SME) and/or superelasticity (SE) for practical applications in devices working at temperatures above 420–470 K [1–8]. In the well-known Ni–Ti-based alloys, the maximum temperature interval for SE is ∼260–370 K [9]. One way to obtain high-temperature SE is increasing the martensitic transformation (MT) temperatures, typically characterized by the M_s point (temperature of start of the direct MT on cooling). In Ni–Ti alloys, high M_s values are reached by alloying a third element, for example Pd, Au, Pt, Hf or Zr [1,2,6,10]. However, the high cost of some of these elements limits the possibility of their use in applications. Another way to achieve high-temperature SE is to expand the temperature interval for the stress-induced MT without significant plastic deformation of the material. In fact, the temperature interval for SE (also denoted as the superelastic window) is related to the strength properties of the austenite phase. Then,

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strengthening the parent phase is a necessary condition to reach high-temperature SE. Precipitation of small and disperse particles is an effective way to strengthen materials (precipitation hardening); in particular, shape memory alloys [2,9]. For instance, precipitation of disperse Ti_3Ni_4 precipitates in Ni–Ti poly- and single crystals with a nickel concentration above 50.6 at.% by ageing treatments in the temperature interval 670–820 K raises the strength properties of the B2 phase, although it does not lead to a substantial increase in the temperatures for SE effect, which do not exceed 370 K [1]. However, the combination of precipitation strengthening and ternary alloying actually leads to high-temperature SE. Indeed, a perfect SE effect up to 490 K with 3% recoverable strain has been recently achieved in a precipitation-hardened $Ni_{50.3}Ti_{29.7}Hf_{20}$ ternary alloy [11].

Co–Ni–Ga alloys with B2-$L1_0$ MT constitute a new class of ferromagnetic materials [12,13] which are widely investigated owing to their unique functional properties of SME and SE [3–5,14–18]. Relatively high levels of strength of the austenite phase can be reached in these alloys by a proper choice of the orientation. In alloys with B2 structure, it is known that dislocation slip takes place along the $\langle 100 \rangle$ direction on $\{110\}$ or $\{100\}$ planes [19]. Then, stressing along the [001] direction leads to a zero Schmidt factor for the operating slip systems, unlike the $[\bar{1}11]$, $[\bar{1}23]$ or [011] directions, in which the Schmidt factors for these slip systems have high values. Therefore, the crystals oriented along the [001] direction should show a wider temperature interval of stress-induced MT in comparison with other single crystal orientations or polycrystals. As a matter of fact, the largest temperature interval for SE in single-phase $Co_{49}Ni_{21}Ga_{30}$ crystals (up to 620 K) has been obtained in [001] oriented samples, in comparison with $[\bar{1}11]$, $[\bar{1}23]$ and [011] orientations [3,4,15–17]. Moreover, Co–Ni–Ga alloys are prone to precipitation of γ' phase (ordered face-centred-cubic (fcc) with $L1_2$ structure) [5,15,20] and the γ' particles seem to strengthen the matrix [15] but, at the present time, the influence of γ' precipitates on the SE effect and its temperature interval is not known in detail. Besides the matrix strength, the disperse precipitated phases also influence the martensitic microstructure developed in thermal or stress-induced MT, depending on the precipitate size, structure and nature (coherent, semicoherent or incoherent) of the matrix/precipitate interface (see, for instance, Refs. [21–23]). The effects originate from the difficulties in accommodating the strain accompanying the MT around the non-transforming particles, which affect the non-chemical energy terms (i.e. elastic and irreversibly dissipative energies) accompanying the MT. For small particle sizes, the whole transformation shear can be accommodated and the growing martensite twins can completely absorb the particles encountered. But for a critical precipitate size, the total transformation strain cannot be accommodated, and then the martensite plates grow in the areas left between precipitates. In this situation, the martensite plate dimensions are not very dependent on the particle size, but on the interparticle distances. The critical particle size depends on different factors such as the amount of misfit between matrix and precipitate lattices, the stiffness of these phases, the amount of MT shear, etc. For the case of γ' precipitates in $Co_{49}Ni_{21}Ga_{30}$ alloys, earlier research work showed that particles having ~3–5 nm in size can be completely absorbed by the martensite twins, but for precipitate sizes of ~10–25 nm the martensite grows in the regions between precipitates, which causes a drastic change of the martensitic microstructure and strongly modifies the thermally induced MT [24].

Usually, the precipitate crystal lattice keeps fixed orientation relationships with the austenitic matrix, and then several orientation variants of precipitates are compatible with the cubic austenitic structure. In many cases, the application of an external stress during the precipitation process is effective in selecting a limited number of precipitate orientation variants. For example, the $Ti_{11}Ni_{14}$ (or Ti_3Ni_4) particles formed in Ni-rich Ni–Ti alloys have an elongated shape with $\{111\}$ habit plane. It was shown in Refs. [25,26] that ageing under tensile or compressive stress along the $[\bar{1}11]$ direction leads to the formation of one variant of precipitates, all oriented on the same (111) habit plane, whereas ageing without stress produces four precipitate variants. The γ' precipitates formed in $Co_{49}Ni_{21}Ga_{30}$ crystals under suitable conditions of ageing temperature and time have an elongated shape with a $\{111\}$ habit plane [15,24]. Then, like in the Ti_3Ni_4 case, it is expected that ageing under stress applied in an orientation close to the $\langle 111 \rangle$ pole will select one variant of γ' precipitates and, in fact, this was initially observed in a previous work [15]. Nevertheless, the effects of elongated nanometric γ' precipitates on the stress-induced MT or the thermally induced MT under stress and the concomitant SME and SE effects have not been systematically studied. This is, therefore, the purpose of the present work. In addition, the influence of the number of orientation variants (one or four) of γ' particles will be reported as well.

2. Experimental procedures

Single crystals of $Co_{49}Ni_{21}Ga_{30}$ (at.%) alloy were grown by the Bridgman technique in alumina (Al_2O_3) crucibles and a helium atmosphere. Samples for compression tests were spark-cut in parallelepiped form with the compression axis oriented along the $[\bar{1}23]$ direction. Such a stress axis has been chosen instead of $[\bar{1}11]$ because it leads to a larger transformation strain. Using the $[\bar{1}23]$ compression axis, the stress component along one specific $\langle 111 \rangle$-type direction is larger than along the other three, and then it is still effective for the precipitate variant selection. It is worth mentioning that the [001] compression axis gives the best performance of $Co_{49}Ni_{21}Ga_{30}$ crystals [3,4,15–17], but such an orientation produces the same stress component along the four $\langle 111 \rangle$-type directions, and then it is not useful for the purpose of the present work.