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Thermal and stress-induced martensitic transformations in NiFeGa single crystals under tension and compression

R.F. Hamilton [a], C. Efstathiou [a], H. Sehitoglu [a,*], Y. Chumlyakov [b]

[a] University of Illinois, Department of Mechanical and Industrial Engineering, 1206 W. Green Street, Urbana, IL 61801, United States
[b] Siberian Physical Technical Institute, Revolution Sq. 1, Tomsk 634050, Russia

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Abstract

Heat treatment and stress state effects on the martensitic transformation in [0 0 1] and [1 2 3] oriented single crystal Ni54Fe19Ga27 alloys are determined. Characteristic temperatures increase for longer aging times and higher hold temperatures. The non-aged [0 0 1] crystals exhibit the smallest stress hysteresis and lowest critical stress in tension. The experimental results are interpreted based on the role of ordering and the second phase on changes in transformation temperatures and hysteresis.

Keywords: Shape memory; Pseudoelasticity; Critical stress; Phase transformation; Ferromagnetic shape memory alloy; Single crystal

1. Introduction

Recently NiFeGa ferromagnetic shape memory alloys (FSMAs) have been discovered to be promising actuator materials [1–5]. Large strain and a rapid response attributed to variant reorientations via twin boundary motion in the martensite are essential to magnetic applications. Ni-rich NiFeGa alloys undergo a thermoelastic transformation from cubic (B2) austenite to tetragonal ($L1_0$) martensite. Oikawa et al. [1–3] found that after heat treatment the high temperature partially ordered B2 structure is transformed into a more ordered $L2_1$ structure during quenching. Oikawa et al. [1] and Omori et al. [4] report that the B2 to $L2_1$ order–disorder transition temperature is near 700 °C. The higher ordered $L2_1$ austenite structure can transform to the $L1_0$ martensitic structure either directly or via intermediate martensitic reorientations. The intermediate martensite may have a seven-layered modulated structure (14M); a five layered modulated structure (10M); or the tetragonal $L1_0$ structure [1,2]. For the ordered NiFeGa alloys, magnetic properties and the martensitic transformation significantly depend on the atomic order of the $L2_1$ phase. Studies have shown that annealing dictates the degree of order of the $L2_1$ phase [1–5]. The studies reveal the influence annealing has on the characteristic temperatures, i.e. the martensite start (M_s), austenite finish (A_f) and Curie (T_c) temperatures. None of the investigations report the affect of annealing on the stress–strain response.

Several works characterized the magnetic response of the thermo-elastic martensitic transformation in this class of alloys after homogenization heat treatments [1–3,5]. Recent works on homogenized and quenched Ni54Ga27Fe19 (at.%) alloys report stress–strain results for ~[1 0 5] oriented single crystals in tension [6] and polycrystals loaded in compression [7]. Sutou et al. [6] observed multiple constant stress plateaus corresponding to multiple stress-induced martensite structures, and observed a single step transformation at the highest test temperature above A_f. They established a critical stress versus temperature diagram for each martensite structure. Masdeu et al. [7] reported compressive results for the polycrystal alloy showing that the critical stress is independent of test temperature above A_f. They concluded that residual martensite stabilizes the

* Corresponding author. Tel.: +1 217 3334112; fax: +1 217 2446534.
E-mail address: huseyin@uiuc.edu (H. Sehitoglu).

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transformation stress in subsequent stress cycles. Their results exhibited multiple martensite structures until the highest test temperature, which displayed linear hardening behavior during the forward transformation. Zheng et al. [8,9] presented DSC results for NiFeGa alloys that exhibited multiple peaks at different temperatures for the "martensitic transformation" and an "intermartensitic transformation". To further the understanding of the stress–strain response of the NiFeGa potential FSMA alloys, the effects of stress state and heat treatment require consideration.

The current work presents the first comprehensive results on the compressive and tensile stress–strain response of [0 0 1](0 1 0) and [1 2 3](4 1 −2) oriented single crystal on aged and unaged Ni54Fe19Ga27 alloys. Aging produces a disordered A1 γ phase that is known to enhance ductility in NiFeGa alloys [4]. Utilizing single crystals circumvents microstructure effects inherent to polycrystals (i.e. internal stresses and grain boundary effects). The chosen orientations represent extremes in the mechanical response for the cubic to tetragonal transformation. Multiple correspondent variant pairs (CVPs) are activated for the [0 0 1] orientation, and a single CVP operates in the [1 2 3] orientation. The material is studied in two conditions: (1) unaged, i.e. after single crystal growth, and (2) aged, i.e. held at temperatures above the order–disorder transition temperature after single crystal growth. Results of differential scanning calorimetry (DSC) experiments provide insight into the thermal induced transformation in the unaged and aged alloys. The characteristic temperatures and thermal hysteresis elucidate the effects of $L2_1$ order. The unaged alloy and the aged alloy (heat treated at 900 °C for 3 h) were chosen for stress–strain analysis because they display the smallest thermal hysteresis and transformation temperatures closest to room temperature. Compressive and tensile stress–strain results distinguish the temperature dependencies of the critical stress and the stress hysteresis and reveal the influence of the stress direction. As a result, a critical stress versus temperature plot is presented that considers asymmetry and heat treatment. The results are instrumental in determining the functionality of this class of materials.

2. Material and experimental results

The alloy investigated was cast to a nominal composition of Ni54Fe19Ga27 (at.%). The single crystals were grown using a Bridgman technique. Compression (4 mm × 4 mm × 10 mm) and dog-bone tension (3 mm × 1.5 mm × 1.3 mm between grips) specimens in the desired single crystal orientations were electro-discharge machined from the cast single crystal ingot. Specimens weighing approximately 80 mg were cut from the compression samples and prepared for DSC. Some specimens were aged for 3 h and 24 h at 900 °C and 1000 °C. Aging induces γ phase that displays inhomogeneous size and inter-particle spacing (Fig. 1). Unaged and aged specimens were thermally scanned at 40 °C/min and the results are presented in Fig. 2. Table 1 gives the characteristic temperatures and thermal hysteresis. Unaged alloys exhibit single peaks for the forward (austenite to martensite) and reverse (martensite to austenite) transformations. As a result of aging, the transformation temperatures increase. Most notably, multiple transformation peaks are induced. Consequently, the

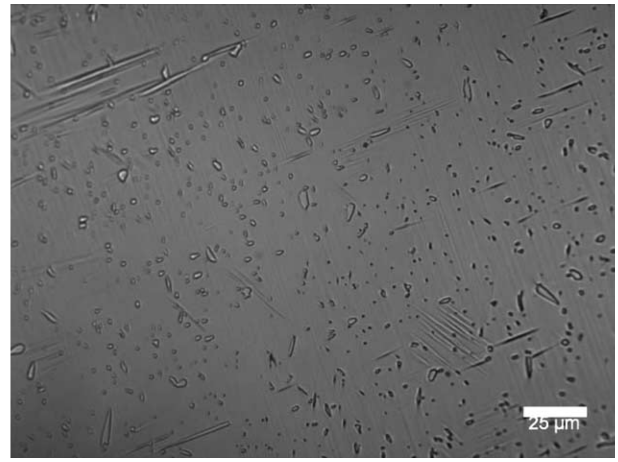

Fig. 1. Optical image of Ni54Fe19Ga27 alloy aged at 900 °C for 3 h. Note the inhomogeneous precipitate size.

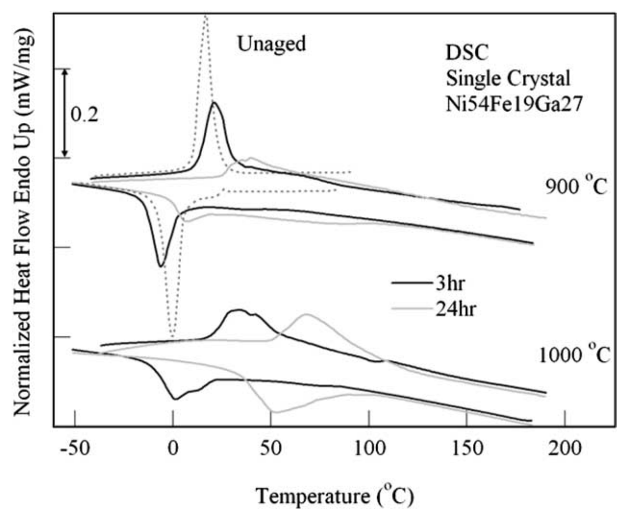

Fig. 2. Differential scanning calorimetry (DSC) results illustrating the effect of aging on the stress-free thermal induced phase transformation.

Table 1
Characteristic temperatures from the DSC results in Fig. 2

Transformation temperatures (°C)					Peak hysteresis (°C)
Heat treatment	M_s	M_f	A_s	A_f	H_T
Unaged	7.0	−8.0	9.0	24.0	16.4
Aged (3 h @ 900 °C)	4.4	−16.0	11.0	30.3	27.7

The peak hysteresis is a measure of the temperature difference between the highest transformation peaks on cooling and heating.

forward ($M_f - M_s$) and reverse ($A_f - A_s$) transformation intervals for the unaged case are on the order of 10 °C and the aged alloys display intervals remarkably higher, up to 100 °C. The unaged alloy exhibits the lowest thermal (~16 °C) hysteresis. After heat treating the specimen for 3 h at 900 °C, the hysteresis only increases by ~12 °C. Observed trends for the hysteresis, characteristic temperatures, and transformation intervals are rationalized in the discussion.

Isothermal stress–strain experiments up to 2% strain were conducted on unaged [0 0 1](0 1 0) oriented single crystals in compression and tension (Fig. 3) and unaged and aged [1 2 3](4 1 −2) crystals in compression (Fig. 4). Mechanical tests were conducted using an Instron servo-hydraulic load frame and strain was measured with a miniature MTS extensometer (3 mm gauge length). Results were obtained via position control. After unloading, complete pseudoelastic recovery was observed for test temperatures above A_f. Near and below M_s, after unloading residual strain remained; therefore, specimens were heated above the A_f temperature to facilitate shape memory recovery. First, the stress–strain response for unaged [0 0 1] oriented single crystals is summarized. Clearly, the modulus for compression (13 GPa) is higher than that of tension (8.6 GPa). Most notably, the transformation becomes elastic at elevated temperatures in compression up to 2% strain. In tension, small transformation stresses, under 10 MPa, occur near M_s, and above A_f, the critical stress barely exceeds 100 MPa, which is considerably lower than that of other ferromagnetic shape memory alloys [9]. For temperatures less than M_s, multiple stress plateaus are observed in tension (−25 and 0 °C) and compression (−25 °C). The results for the [1 2 3] oriented single crystals in Fig. 3 illustrate the effect of heat treatment. For the [1 2 3] orientation, the moduli of the unaged (30 GPa) and aged (50 GPa) alloys are significantly higher than the [0 0 1] case. The increased strength and modulus of the parent phase suggests microstructure strengthening mechanisms are operative that we expound on later.

The temperature dependence of the critical stress is presented in Fig. 5. Note that the M_s and A_f temperatures on the plot are those of the unaged alloy. Above M_s, contrasts in the slopes are noticeable. In tension, the [0 0 1] oriented single crystals exhibit a lower slope compared to compression, and the slope of the unaged [1 2 3] orientation is larger than both stress states. The critical stresses are equivalent for the aged and unaged [1 2 3] single crystals for 25, 50, and 75 °C; however, those of the aged specimens become higher when permanent plastic deformation remains. The stress hysteresis provides qualitative insight into dissipative mechanisms (i.e. frictional dissipation and plastic relaxation) associated with the stress-induced transformation. In the unaged condition, the hysteresis is on the order of 10 MPa for each orientation and stress direction. After aging for 3 h at 900 °C, the hysteresis of the [1 2 3] oriented single crystals increases dramatically (~70 MPa)

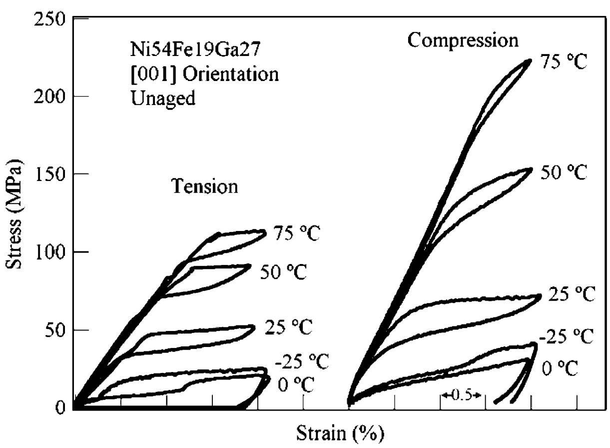

Fig. 3. The influence of stress direction on the stress–strain response.

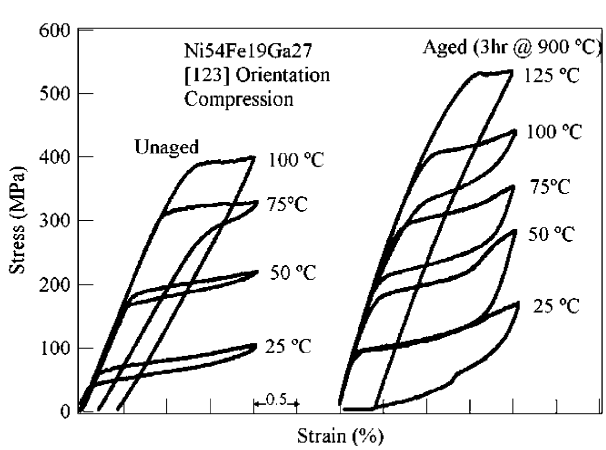

Fig. 4. The influence of heat treatment on the stress–strain response. Note the stress scale is different than that of Fig. 3.

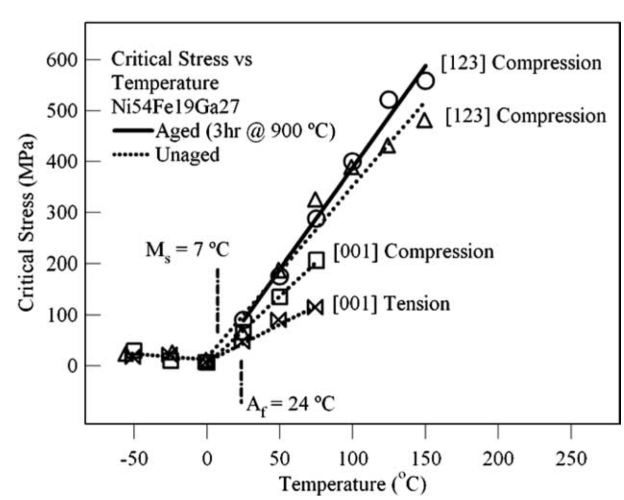

Fig. 5. Temperature dependence of the critical stress for the initial martensitic transformation. The transformation temperatures correspond to the unaged condition.

compared to the unaged alloy. The preceding observations are rationalized in the discussion.

3. Discussion of results

Characteristic temperatures increase with longer aging times and increasing aging temperature which corresponds with the results of Oikawa et al. [1,3]. Oikawa et al. asserted that the degree of order of the $L2_1$ parent phase decreases for aging temperatures closer to the $B2/L2_1$ (~700 °C) ordering temperature creating antiphase domains (APDs) and the transformation temperatures increase [1,3]. The current aging temperature, 900 °C, is above the ordering temperature and we expect APDs with less order, having less order than the unaged $L2_1$ parent phase, for the short 3 h aging time. The γ phase and the APDs create a heterogeneous microstructure that yield the strikingly different mechanical response for the aged alloy.

Ling and Owen [10] provided a very insightful discussion pertaining to the effect of ordering. They noted that the driving force at M_s depends on the degree of order, and that M_s increases for alloys with less order. The multiple transformation peaks and larger transformation temperature intervals for the aged alloys provide evidence that antiphase domains exist in the aged alloys in the current study. The antiphase domains create local disruption of order in the microstructure that changes the driving force for the transformation locally. Consequently, the martensitic transformation occurs at different temperatures in different areas depending on the local atomic ordering. The hysteresis also increases for alloys with less order according to Ling and Owen. The stress and thermal hysteresis did in fact increase for the aged alloy compare to the unaged condition. Frictional dissipation contributes to the hysteresis, and the creation of APDs increases the hysteresis likely due to increased frictional dissipation. In addition the stress hysteresis may be increased if internal stresses resulting from the APDs induce certain martensite CVPs that interact with those oriented to the external stress thus enhancing plastic relaxation and/or frictional dissipation [11,12].

Wagoner Johnson et al. asserted that heterogeneity of precipitate size and inter-particle spacing alters the thermo-mechanical driving force locally, causing multiple-DSC peaks and broad transformation intervals [13]. Indeed, the heterogeneous aged microstructure in the Ni54Fe19Ga27 alloy causes similar DSC behavior. The internal stress fields of the γ phase will induce martensite variants that interact with external stress-induced martensite thus increasing the hysteresis as stated in the previous paragraph.

Permanent deformation, which first occurs at 125 °C for the aged alloy, first occurs at 75 °C for the unaged alloy, and the aged alloys display a larger pseudoelastic window. The ductility enhancement attributed to the γ phase increases the pseudoelastic window. Evidently, the extra energy associated with APDs may assist the reverse transformation thus enhancing pseudoelasticity at higher temperatures. The fact that critical stresses for the same temperature are similar for the aged and unaged cases suggests that the order and secondary phase microstructure are indeed inhomogeneous. Otherwise, if the aged alloy was homogeneously ordered differently from the unaged alloy and the secondary phase size and inter-particle spacing were homogeneous, the stresses would differ.

The stress–strain results for the Ni54Fe19Ga27 alloys (Figs. 3–5) illustrate that the stress-induced martensitic transformation in this class of alloys exhibits a strong dependence on stress state and single crystal orientation. Tension–compression asymmetry is significant for the [0 0 1] orientation. Remarkably, the compressive response becomes elastic at temperatures higher than A_f, even though a critical stress and stress plateau are obvious in tension. The parent phase elastic moduli for the [0 0 1] orientation exhibit asymmetry since the elastic modulus for compression is higher than that for tension. The tension–compression asymmetry of the critical stress (Fig. 5) indicates that the resolved shear stress of the martensite variants induced in tension is higher than that of those induced in compression.

It is well-known that the preferred variants that are induced depend on the stress state and can have different orientations giving rise to such asymmetry [12]. For temperatures near (0 °C) and below M_s (−25 °C) multiple stress plateaus exits in tension at low stresses. In compression, multiple transformations occur significantly below M_s, at −25 °C, and there is no flat stress plateau. This reveals that the martensite deformation and rearrangement occurs through different mechanisms for tensile and compressive stresses. The Clausius–Clapeyron relation exhibits a higher slope for the [1 2 3] orientation compared to the [0 0 1] orientation, which is attributed to the differences between single CVP formation versus multiple CVP formation. Similar to slip, the multiple CVPs make the [0 0 1] orientation a softer orientation and this creates the higher elastic modulus observed for the [1 2 3] orientation. Comparing Figs. 3 and 4, the austenite is clearly more stable for the [0 0 1] orientation since the behavior tends toward an elastic response. The results indicate that the effect of stress state and orientation on the stabilization of austenite deserves further study in these highly ordered alloys.

4. Conclusions

1. For the first time, the stress-induced transformation is characterized for Ni54Fe19Ga27 alloys in tension and compression and mechanical results are obtained in the presence of the A1 disordered γ phase. The results demonstrate that the stress mode significantly influences the stress–strain behavior of the austenite elastic modulus and the deformation and reorientation of martensite during the transformation.

2. Tension–compression asymmetry of the critical stress and elastic modulus exist for the unaged [0 0 1] single crystals indicate that different martensite variants are selected for different stress states. Consequently low critical stresses can be obtained in tension with considerably higher transformation strains than compression.
3. For the cubic to tetragonal phase transformation, the [0 0 1] orientation has multiple active CVPs, hence its ductility is enhanced. Conversely, the modulus increases for the [1 2 3] orientation because a single CVP is activated. Crystallographic orientations with multiple active CVPs enhance ductility and cut the critical stress in half, due to the lower modulus, near M_s. Ductility is enhanced in the aged case due to the γ phase and this is reflected by the increased pseudoelastic window.
4. Heat treatments at temperatures above the order–disorder transition temperature for short times create antiphase domains with less order than the unaged $L2_1$ parent phase. This introduces microstructure heterogeneity that locally influences the driving force for the transformation. In addition to the APDs, the microstructural heterogeneity is enhanced by the γ phase. As a result the transformation temperatures, the DSC transformation intervals, and the thermal and stress hysteresis increase. Atomic ordering of the parent phase can be manipulated through heat treatment to obtain the desired M_s, critical stress, hysteresis, and strength properties.

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