Stress-Strain-Temperature Behavior of [001] Single Crystals of Co49Ni21Ga30 Ferromagnetic Shape Memory Alloy under Compression

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Stress-Strain-Temperature Behavior of [001] Single Crystals of Co$_{49}$Ni$_{21}$Ga$_{30}$

Ferromagnetic Shape Memory Alloy under Compression

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Keywords: CoNiGa; Martensitic phase transformation; Ferromagnetic shape memory alloy; Microstructure; Deformation behavior.

Abstract

The conventional shape memory effect (SME) and pseudoelasticity (PE) in as grown [100] single crystals of Co$_{49}$Ni$_{21}$Ga$_{30}$ alloy under compression are reported. The parent single crystals exhibit about 5% transformation strain at compressive stress levels as low as 4 MPa, and a pseudoelastic strain of 4.5%. Complete PE was observed in the temperature range from 35 to 285 °C, along with increasing stress hysteresis with temperature. The latter is attributed to increasing number of variants and the corresponding variant-variant interactions. We demonstrate that the current material can be utilized in applications that demand high strength at elevated temperatures. Moreover, the current results also indicate the potential of this material to exhibit magnetic shape memory effect, which could broaden the scope of utility of this material upon further research.

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Motivation and Significance

Ferromagnetic shape memory alloys (FSMAs) are currently under the focus of many studies, owing to their rapid cyclic actuation at frequencies in the order of few hundreds of Hz [1], their ability to absorb large vibration energy [2], and the viability of polymer/FSMA composites as energy absorbers [3]. This class of materials exhibit large magnetic field-induced reversible strains (up to 10 %) [4] and reorientation-induced magnetization [5], promoting their use in actuator and sensor applications.

The underlying mechanism of the large magnetic field-induced strain (MFIS) exhibited by FSMAs is either the field-induced phase transformation [6-13], or the field-induced twin boundary motion [6, 12-14]. In either mechanism, the magnetic driving force originating from magnetocrystalline anisotropy energy (MAE) difference in the case of weak anisotropy (or the Zeeman energy difference in the case of strong anisotropy) across the twin or phase boundary needs to overcome the stress required to propagate the twin or phase front [6, 13]. Therefore, in order to fully comprehend magneto-thermo-mechanical characteristics of these alloys, it is crucial to fully understand thermo-mechanical behavior of FSMAs, specifically the thermally and stress-induced phase transformations, critical stress for twinning, stress and thermal hysteresis evolution, and twin boundary mobility at different temperatures.

A considerable amount of research has been conducted on several FSMA systems, including NiMnGa [1-10], NiFeGa [11], FePd [12, 15-17], Fe₃Pt [15, 17] and FeCoNiTi [17-21]. Nevertheless, their utility in practical applications is still limited owing to their extreme brittleness in the polycrystalline state, their high cost of constituent elements, or poor performance under the desired circumstances [22]. This has prompted the scientists to fabricate new high-strength Heusler-type ferromagnetic materials, which are ductile and exhibit reversible martensitic transformation [23].

Newly developed Co-based FSMAs, such as Co-Ni-Al [13, 22, 24-26, 39-40] and Co-Ni-Ga [22, 27-30] display promising mechanical properties for both conventional and
magnetic shape memory applications. The material of interest in this study is a Co-Ni-Ga alloy, with 21 at.% Ni, 30 at.% Ga and balance Co. The Co-Ni-Ga system was chosen due to the hot-workability, good room temperature ductility [22, 31], high strength, low density, high melting point, and good corrosion resistance, which provide a venue for their utility in practical applications.

The Co-Ni-Ga ternary system with the $\beta$-phase covers a wide range of compositions capable of undergoing a thermoelastic martensitic transformation upon cooling [28, 29]. It is important to note that the magnetic properties of the Co-Ni-Ga $\beta$-phase alloys are very similar to those of the Co-Ni-Al $\beta$-phase alloys [22, 26], implying that the Co-Ni-Ga alloys possess large MAE, as in the case of Co-Ni-Al alloys. Moreover, the chemical composition utilized in this study gives way to a relatively high Curie temperature (>120 °C) and a relatively low martensite start ($M_s$) temperature (-20 °C) [22]. This increases the room-temperature saturation magnetization, which in turn leads to increased Zeeman energy difference, which is necessary for moving the twin and/or phase boundaries [32]. Subsequently, the large gap between the transformation temperatures provides a wider operational temperature range for the magnetic shape memory effect (MSME) [9]. Also note that the critical electron per atom (e/a) ratio of about 7.4 and the chemical composition of the alloy studied fulfils the condition for CoNiGa alloys to exhibit both conventional shape memory effect (SME) and MSME*, based on the studies carried out on alloys with various chemical compositions [27, 28]. Nevertheless, there are only few studies available that focus on the thermo-magneto-mechanical characteristics of CoNiGa. So far, the field assisted/controlled shape memory and two-way shape memory effects [31, 33, 34], and the composition dependency of martensitic transformations [28, 30, 35] in this class of alloys were investigated. Moreover, the stress-strain response was shown to display strain-induced martensite stabilization, and Clausius-

* The term magnetic shape memory effect (MSME) has been widely used in the literature, however different authors associate different meanings with it, including magnetic field-induced phase transformation and variant reorientation. In this paper we associate the term MSME with magnetic field-induced phase transformation.
Clapeyron relation was also established [36, 37] for this FSMA system. Nonetheless, conventional SME, pseudoelastic response, and mechanical behaviour of CoNiGa alloys have not been fully explored yet.

The current paper presents the conventional SME and pseudoelasticity (PE) in as grown Co-Ni-Ga [001] single crystals under compressive loading. The [001] single crystal orientation was selected in order to curtail the dislocation activity in the parent phase, as the \{110\} <100> slip is usually prevalent in B2 crystals [19, 38]. Thereby the influence of dislocation slip in austenite on the formation of stress-induced martensite (SIM) is minimized. We also report on the change in transformation strains and thermal hysteresis due to varying applied stresses, and lattice resistance to twin boundary motion and its temperature dependency. Moreover, the effects of applied strain history and temperatures on the critical stress levels and stress hysteresis were investigated, and magnetization response of austenite and martensite under external magnetic fields are reported.

Experimental Techniques and Results: Conventional SME and Pseudoelasticity

The material studied is a Co-Ni-Ga alloy with 21 at.% Ni, 30 at.% Ga, and balance Co, referred to as CoNiGa in the remainder of the text. The material possesses a B2 structure at room temperature [27]. Single crystals were grown in a He atmosphere, utilizing the vertical Bridgman technique. Compression samples with dimensions of 4 mm × 4 mm × 8 mm were extracted from the single crystals by electro-discharge machining (EDM), such that the compression axes coincide with the [001] crystallographic orientation. The transformation temperatures were determined through differential scanning calorimetry (DSC) (Figure 1). Accordingly, the austenite start ($A_s$), austenite finish ($A_t$), $M_s$ and martensite finish ($M_f$) temperatures are -2.4, 1.3, -18 and -22.4 °C, respectively (Figure 1). A stress-free thermal hysteresis of about 20 °C is present in this material.
The mechanical tests were carried out on servohydraulic test frames. Strain measurement was accomplished with the aid of a high-temperature extensometer with ceramic extension rods and a gauge length of 12 mm, attached to the compression plates. Depending on the test temperature range, heating/cooling was either achieved by direct flow of hot/cold nitrogen gas onto the samples or by induction heating for test temperatures above 200 °C. The heating/cooling rate was limited to 10 K/min, and thus, temperature variation along the sample could be kept to a maximum of ± 2 °C. Two types of mechanical tests were conducted to study the transformation behavior of the alloy: Constant stress temperature variation experiments, and isothermal incremental strain tests.

The strain-temperature response of [001] oriented CoNiGa single crystals under constant compressive stress (Figure 2) revealed that the phase transformation occurs in a rather abrupt manner at low stress levels (e.g. ~4 MPa), accompanied by a low thermal hysteresis. Yet higher levels of applied compressive stresses bring about a completely different picture, such that a wider thermal hysteresis is present (Figure 2). Furthermore, both the transformation strain and temperature hysteresis evolve with externally applied stress. The increase in thermal hysteresis is not drastic above stress levels of 50 MPa, and the saturation is reached at 150 MPa and higher stresses. The transformation strain of 4.7% at 4 MPa applied stress decreases with increasing stress levels, converging to a saturation value of 3.5% at applied stress levels of 150 MPa and above. The critical stress for each cycle (Figure 3) was determined by employing the intersecting slopes method [41].

In order to investigate the potential MSME in the CoNiGa alloy studied, we observed the magnetization response of the [001] oriented single crystals (Figure 4). A Superconducting Quantum Interference Device (SQUID) magnetometer was utilized for determining the magnetization response of the material [39]. Based on the DSC measurements (Figure 1), the samples were subjected to a magnetic field at two different temperatures,
namely -53 °C and 27 °C (Figure 4), in order to establish the differences between martensite and austenite, respectively.

**Interpretation of Experimental Results**

The cyclic temperature experiments carried out under various constant stress levels (Figure 2) revealed that the phase transformation takes place abruptly at lower applied stress levels (-4 MPa). Such transformation behavior suggests the nucleation of a single active correspondent variant pair (CVP) at these stress levels, which grows into a single variant, thereby reducing the interaction between the CVPs [42, 43]. Based on this argument, we can state that the CoNiGa alloy exhibits a low variant reorientation stress (<4 MPa) [8, 10], which is a necessary condition for achieving magnetic field-induced strains (MFIS) by twin boundary motion under external magnetic fields [8, 10]. Moreover, an external stress of about -4 MPa gives way to a transformation strain of about 4.7%, which is the transformation strain from single crystal austenite to single crystal martensite. Thus the reorientation stress level (or the twinning stress level) has to be less than 4 MPa. We note that a minimum compressive stress of about 4 MPa is needed for adequate and secure positioning of the specimen between the compression plates.

As for the higher stress levels (150 MPa), however, the transformation does not occur abruptly, but takes place in a gradual manner (Figure 2) due to the difficulty in forward transformation brought about by the increased interaction between the thermally-induced and stress-induced martensitic variants, and this is valid for even higher temperatures. Figure 5, which illustrates martensitic variants grown in several directions, shows an example to this statement, where interaction between these differently oriented martensitic variants takes place. Consequently, the martensite is expected to possess a partial self-accommodating structure at these stress levels, where thermally- and stress-induced variants coexist. This is supported by the observed decrease in transformation strain with increasing stress level.
(Figure 2). On the other hand, the increase in thermal hysteresis is associated with the mechanical stabilization of martensite, leading to the reverse transformation at elevated temperatures [44]. We also note that the current data (Figure 2) fits the Clausius-Clapeyron equation with a slope of 1.9 MPa/K [45]. Further elaboration, such as in-situ observations of the microstructural changes, is necessary in order to draw a solid conclusion regarding this point.

In addition, $M_s - M_f$ and $A_f - A_s$ difference becomes wider at higher stress levels (Figure 2), demonstrating the difficulty of phase front propagation at these stresses. This difference in strain-temperature response due to change in applied stress levels stems from the fact that the frictional dissipation during phase transformation increases with increasing external stresses. We also would like to note that the difference between the transformation temperatures obtained from DSC and strain-temperature experiments results from a possible heterogeneity in the chemical composition. Specifically, the samples utilized in DSC are much smaller in size compared to the specimens used in strain-temperature tests. While the large specimens reflect the average response, even a small inhomogeneity in the composition could lead to bigger effects in a small DSC sample. Moreover, the material utilized in this study was as-grown, and this could cause inhomogeneities in the bulk.

The pseudoelasticity experiments (Figure 3) lay out a few points that deserve further attention. To begin with, the [001] oriented single crystals exhibit complete pseudoelasticity at both low (Figure 3(a)) and high (Figure 3(b)) temperatures. These single crystals display about 4.5% pseudoelastic strain accompanied by a relatively small stress hysteresis, namely less than 30 MPa at lower temperatures, and not more than 200 MPa at elevated temperatures (Figures 3(a) and (b)). Despite the difference in the magnitude of the stress hysteresis between low and high temperatures, one common feature is that the hysteresis becomes larger with increasing stresses/strains achieved in each loading cycle. Moreover, this increase in the magnitude of the stress hysteresis is accompanied by serrations in the flow curve, such that
the serrations become more pronounced with increasing number of loading cycles, i.e. with increasing stresses/strains, and this phenomenon is more significant in the case of elevated test temperatures (Figure 3(b)). As both the temperature and applied stress levels increase, the number of active variants increases, and thereby more variant-variant interactions take place, bringing about local stress increases/drops, which give way to the increase in serrations [41, 46]. In addition, the large hysteresis of about 200 MPa with a 4% recoverable strain at elevated temperatures (Figure 3(b)) is clearly indicative of large frictional dissipation during the transformation of SIM.

The second important observation regarding the pseudoelastic response (Figure 3) is that an ascending stress-strain curve is exhibited by the single crystals studied. This suggests that the SIM is characterized by a partial self-accommodating structure (Figure 5), accompanied by nucleation of multiple variants, which also give way to the aforementioned stress hysteresis/serration response. The ascending stress-strain response is more pronounced at elevated test temperatures (Figure 3(b)), accompanied by a reduction in critical stress to induce SIM after several PE cycles. We postulate that this stems from the martensite stabilization or easy growth of trained variants supported by local stress fields induced after each cycle.

Moreover, the incremental strain test results revealed that, at lower temperatures (35 °C), the critical stress level does not change (Figure 3(a)), whereas a notable -yet not drastic-decrease in the critical stress levels (Figure 3(b)) is prevalent at higher temperatures (225 °C) due to increasing strains. What is noteworthy is that there is about a four-fold increase in the critical stress levels solely due to the increase in test temperature (Figure 3). Interestingly, the response at low stress levels differs significantly from that observed in [001] oriented CoNiAl single crystals [39, 40], indicating expressively lower critical stress levels for the CoNiGa alloy in comparison to CoNiAl.
The magnetization experiments revealed a noticeable Zeeman energy difference (shaded area in Figure 4) between austenite and martensite, which serves as the driving force for phase transformation. Whether the external magnetic field application triggers the martensite to parent phase transformation, or the opposite, depends also on the MAE, and the (simultaneously) applied stress field. Moreover, the Zeeman energy difference depends on the chemical composition and temperature, yet our measurements were taken at different temperatures for martensite and the parent phase (Figure 4). Therefore, at this point, we only note the possible MSME capability of the CoNiGa alloy based on the magnetization response difference between the two phases, yet do not draw a solid conclusion regarding the MSME properties of this alloy, which is beyond the scope of the current work. A detailed investigation on the MSME properties of the current CoNiGa alloy is underway.

We have shown that the CoNiGa alloy is capable of exhibiting complete pseudoelasticity and SME both at high and low temperatures. Moreover, we have also demonstrated that this alloy has a potential to display MSME, based on the conventional shape memory properties and preliminary magnetization response. Although the current results clearly show that this alloy definitely constitutes an alternative to other shape memory alloys utilized in high temperature applications, more elaboration is needed regarding both the magnetic and cyclic properties of the CoNiGa alloy prior to its utility. Thus, work is currently underway to establish the magnetic properties of this material in correlation with its conventional shape memory properties.

Conclusions

The conventional shape memory effect (SME) and pseudoelasticity (PE) in as grown Co-Ni-Ga (CoNiGa) [001] single crystals under compressive loading were reported. Moreover, the magnetization responses of austenite and martensite were also monitored. We draw the following conclusions from the work presented herein:
1. The [001] single crystals exhibit about 5% transformation strain at compressive stress levels as low as 4 MPa, and a 4.5% pseudoelastic strain. Complete pseudoelasticity was observed in the temperature range from 35 to 285 °C.

2. The increase in stress hysteresis due to increasing temperature is attributed to increasing number of variants and the corresponding variant-variant interactions. The increase in temperature and applied stress levels brings about an increase in the number of active variants, and thereby higher possibility for variant-variant interaction, leading to local stress increases/drops, which give way to the increase in stress hysteresis and accompanying serrations in the flow curve.

3. The CoNiGa alloy exhibits SME, PE and the conventional shape memory properties of this alloy and the preliminary observations of the magnetization response point at its capability to display magnetic shape memory effect (MSME), providing a venue for its utility in applications that demand MSME and high strength at elevated temperatures.

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References


Figure Captions

Figure 1. DSC curve of CoNiGa alloy, showing the $A_s$, $A_f$, $M_s$ and $M_f$ temperatures, and the thermal hysteresis ($T_H$) brought about by stress-free thermal cycling.

Figure 2. Isostress strain-temperature behavior of [001] oriented CoNiGa single crystals. The scale bar on the strain axis is used instead of a conventional scale to avoid misunderstanding as the curves were shifted vertically from their original position for the sake of a clear presentation.

Figure 3. Incremental strain test on the [001] oriented CoNiGa single crystals displaying the influence of temperature: (a) 35°C and (b) 225°C. Note the scale difference between the y-axes of (a) and (b). The tables cite the corresponding critical stresses for each cycle.

Figure 4. The variation in magnetization with temperature under external magnetic fields. The shaded area represents the Zeeman energy difference.

Figure 5. The residual martensite plates that grew in different directions in a deformed sample. This sample was deformed to and failed at 4% strain, at 285 °C. The micrograph was taken after cooling down to room temperature.
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$450x245mm$ $\left(72 \times 72 \text{ DPI}\right)$
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237x281mm (72 x 72 DPI)
Figure 4. The variation in magnetization with temperature under external magnetic fields. The shaded area represents the Zeeman energy difference.

Magnetization Curves for Co$_{49}$Ni$_{21}$Ga$_{30}$

-53 °C

27 °C

Magnetization, emu/g

Magnetic Field, Oe

- 450x245mm (72 x 72 DPI)
Figure 5. The residual martensite plates that grew in different directions in a deformed sample. This sample was deformed to and failed at 4% strain, at 285 °C. The micrograph was taken after cooling down to room temperature.

128x87mm (600 x 600 DPI)