Transformation of Co–Ni–Al single crystals in tension

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Abstract

We present for the first time pseudoelasticity and shape memory results on Co–Ni–Al single crystals in tension. The experimental transformation strains approached 6% in tension in the [1 1 5] orientation. Despite the considerable volume change (0.0447), the transformation exhibits remarkable pseudoelasticity and shape memory recoverability in tension. A theoretical treatment is presented to explain the tension compression asymmetry in the stress–strain response, the change in transformation hysteresis with stress, and the role of secondary phase on the transformation temperatures.
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1. Introduction

The present investigation is aimed at developing an understanding of the stress-induced martensitic transformation in Co–Ni–Al under tension. There has not been previously published work on shape memory behavior of single crystals in tension in this class of alloys [1,2]. A noteworthy difference between the Co–Ni–Al and the other well known shape memory alloys is the substantial positive volumetric change (~4.47%) that biases tension–compression asymmetry and transformation temperatures. Previous investigations on other shape memory alloys of the Ni- and Cu-variety have noted that the volumetric changes are rather small (<0.3%) [3], and it has been accepted that a small volumetric strain ensures that the transformation proceeds with limited plastic deformation and a large degree of reversibility. The Co–Ni–Al alloys present somewhat of an anomaly because large recoverable strains are achieved in experiments (maximum of 6% in tension in the [1 1 5] direction) despite the presence of a substantial volumetric strain. The use of single crystals facilitates the achievement of large strains [4] and permits a closer examination of recoverability in these alloys.

Shape memory investigations in the literature have been confined to compression [4–9]. With suitable heat treatments on single crystals we optimize the transformation temperatures, produce a two phase microstructure, and obtain large strains in tension. We present these new findings for single crystals in the [1 1 5] orientation. The choice of [1 1 5] orientation allows large strains in tension while circumventing the lack of slip (hence brittle behavior) in [0 0 1] direction. A simple thermodynamic framework is presented that predicts the shift in transformation temperatures with external stress. Similar to our previous studies, the energy

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minimization (EMT) [10] and lattice deformation [11] (LDT) theories are used to establish the transformation strains in understanding the orientation dependence.

A range of compositions in Co–Ni–Al is capable of producing this transformation and depending on the heat treatment, a second phase develops that promotes ductility [4–9]. The γ second phase is a ductile A1 disordered face-centered-cubic phase that forms a lamellar eutectic-like microstructure [6–9]. The transformation temperatures, particularly M_s, can be individually controlled in the range of −150 °C to 250 °C by changing the composition of Co and Al [6,7]. The compositional limits for Co–Ni–Al are such that Al can vary from 20 to 30 at.% [1,6,7,9]. Advantages of these alloys include selecting a M_s temperature with compositional changes and heat treatment, pseudoelastic response at room temperature and at higher temperatures, and shape changes under applied magnetic fields.

The current study also presents a complete theoretical solution of the transformation strains for tension. The growth of the martensite from the most favorably oriented correspondent variant pair (CVP) was calculated. The role of detwinning, to obtain a single crystal variant of martensite, on the transformation strains is also identified. The role of detwinning is nearly 3.5% in tension for the [1 1 5] orientation. This information has not been presented in previous studies and points out the potential of Co–Ni–Al alloys for high transformation strain applications. Thermomechanical modeling based on the complimentary free energy is included to rationalize the shift in transformation start temperatures in the presence of the second phase as well as the role of the large volumetric strain. The current approach is a modification of Hamilton et al. [12] to rationalize the stress dependence of the hysteresis in NiTi single crystals by incorporating elastic strain energy relaxation due to dislocation emission at the transformation interface. With this background, the purpose of the present investigation of Co–Ni–Al is:

(i) to determine the experimental transformation stresses, strains, and temperatures in tension on [1 1 5] oriented single crystals,
(ii) to present theoretical calculations of transformation strains in tension and compare them to the experimental results,
(iii) and to demonstrate the shift in transformation temperatures and volumetric strain using a theoretical approach.

Overall, we demonstrate that Co–Ni–Al alloys have superior mechanical properties compared to a number of other ferromagnetic shape memory alloys. These alloys can be heat treated to have a secondary phase which raises the fracture resistance, a critical requirement for large transformation strains in tension.

2. Theoretical considerations

2.1. Recoverable strains

For the cubic (B2) to tetragonal (L1$_0$) martensitic transformation, there are three independent lattice correspondences [11,13]. Two correspondent variants in twin relation to one another constitute a CVP and 24 CVPs exist for the martensitic transformation in this class of alloys. Several recent works have implemented the energy minimization method (EMT) [10] to predict the orientation dependence of CVP strains for Ni–Ti [14,15], Fe–Ni–Co–Ti [13,16], and Co–Ni–Al [5]. In the present work, the habit (invariant) plane orientations, transformation directions, and the twin parameters are established for Co–Ni–Al with the lattice parameters $a_0 = 2.85$ Å [6], $c = 3.185$ Å, and $a = 3.897$ Å established based on X-ray diffraction. The twin plane and twin shear vectors are $\boldsymbol{n} = (0, 0.70711, 0.70711)$, and $\boldsymbol{a} = (0, 0.19665, 0.22729)$. The volume fraction of variants in a CVP is $f = 0.2345$ and $1 - f = 0.7655$. Finally, the habit plane normal and transformation directions are established as $\boldsymbol{m} = (−0.52914, 0.04111, 0.84753)$ and $\boldsymbol{b} = (0.06498, 0.00452, 0.09313)$, respectively.

Recoverable strains in excess of CVP strains are accumulated due to detwinning and are determined using the LDT formulation originally proposed by Saburi and Nenno [11]. Detwinning refers to the conversion of the favorably induced martensite CVP to a single crystal variant (SCV). The SCV strain minus the CVP strain is the contribution from detwinning. For the LDT, the lattice correspondences are used to determine the deformation gradient, and the coordinate transformation $F'_{ij} = R_{ik}F_{kl}R_{jl}$ is implemented to move to the parent coordinate system and excludes rigid body rotations. The large (Green) strain theory is then used to calculate transformation strains using

$$\varepsilon_{ij} = \frac{1}{2}\left(F'_{ki}F'_{kj} - \delta_{ij}\right)$$
$$= \frac{1}{2}\left[\boldsymbol{b} \otimes \boldsymbol{m} + \boldsymbol{m} \otimes \boldsymbol{b} + (\boldsymbol{b} \bullet \boldsymbol{b})\boldsymbol{m} \otimes \boldsymbol{m}\right] \quad (1)$$

We note that the CVP formation strain (of the most favorably oriented correspondent variant pair) is as high as 7.79% in tension, and the CVP + detwinning strain is 11.28%. Contour plots summarizing the transformation strains for all orientations are given in Fig. 1. The [1 1 5] orientation of interest in this study is marked. The transformation strains near the [1 1 1] pole are very small, the [0 0 1] is the highest and [0 1 1] is intermediary. Note that $\boldsymbol{b}$ is not a unit vector and the magnitude of the transformation is determined as $|\boldsymbol{b}| = 0.114$. Although the transformation magnitude is lower than in conventional SMAs such as CuZnAl (0.23) [3], FeNiCoTi (0.1823) [16], and NiTi (0.1300) [14], the volumetric strain is
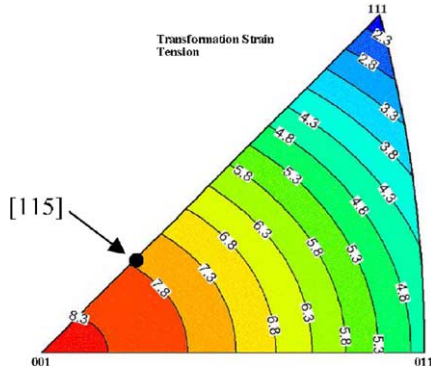
Fig. 1. Contours of transformation strain in tension. The [1 1 5] orientation is marked on the figure.

nearly 4.47%, which is considerably greater than the volume change in those alloys. Consequently, the Co–Ni–Al alloys experience a significant extension normal to the habit plane in tension that is rather small in thermoelastic martensitic transformations. The volume change is comparable to that of carburized steel (+4%) [17], yet significant recoverable strain persists in the Co–Ni–Al single crystals. This anomaly is a remarkable finding that has yet to be studied further in this class of alloys.

We now highlight the influence of the positive volume strain. The external stress can be resolved parallel (τ_0) to and perpendicular (σ_0) to the habit plane and the transformation strain ε_{ij}^n can be separated into deviatoric and volumetric components as $\varepsilon_{ij}^n = \varepsilon_{ij}'^n + \frac{1}{3}\delta_{ij}\varepsilon_{kk}^n$. Considering the strain energy as $U = \sigma_0\varepsilon_0/3 + \tau_0\varepsilon_0'$ [18], we note that the deviatoric (second) term will always be positive as the shear stress and strain are of the same sign. The volumetric (first) term, however, will be positive in tension as the normal dilatation is always positive. Consequently, the strain energy in tension is greater than in compression facilitating the transformation in tension while promoting plastic accommodation at the austenite/martensite interfaces.

2.2. Transformation temperatures

The thermomechanical model outlined by Hamilton et al. [12] clarifies the influence of irreversibilities and we use it to consider how the γ phase and the large volumetric strain modify the transformation behavior. The local thermodynamic driving force for the transformation is obtained from partial differentiation of the complimentary free energy with respect to the martensite variant volume fraction [3,12,19,20] yielding

$$F^n = -B(T - T_0) + \sum_n \Sigma_{ij}\varepsilon_{ij}^n + \sum_n \left(\sigma_{ij}^{\gamma\text{-dist}}\right)^n \varepsilon_{ij}^n$$
$$+ \frac{\partial}{\partial f^n}\left[\frac{1}{2V}\int_\Omega \sigma_{ij}^{\text{m-dist}}\varepsilon_{ij}^{\text{dist-tr}}\,\mathrm{d}V\right] \qquad (2)$$

The $\varepsilon_{ij}^{\text{dist-tr}}$ and $\varepsilon_{ij}^{\gamma\text{-dist}}$ terms are the local disturbance strains due to the transformation and mismatch strain associated with the γ phase respectively. Similarly, the $\sigma_{ij}^{\gamma\text{-dist}}$ and $\sigma_{ij}^{\text{m-dist}}$ terms are the disturbance stresses due to the γ phase and martensite respectively. The last term is an interaction energy term that represents a barrier to the forward transformation. Considering the transformation of only one favorably oriented variant, we can ignore the interaction term. To determine the effects of the large volumetric strain in Co–Ni–Al, we use the deviatoric and volumetric components of the transformation strain, and the martensite start temperature as a function of external and internal stress is,

$$M_s = T_0 + \frac{1}{B}\left[\Sigma_{ij}\left(\varepsilon_{ij}'^n + \frac{1}{3}\delta_{ij}\varepsilon_{kk}^n\right)\right.$$
$$\left. + \left(\sigma_{ij}^{\gamma\text{-dist}}\right)^n\left(\varepsilon_{ij}'^n + \frac{1}{3}\delta_{ij}\varepsilon_{kk}^n\right) - F_c\right] \qquad (3)$$

Irreversibilities due to interfacial friction and defect generation are accounted for in a phenomenological way using the critical driving force F^c. The role of secondary phases is reflected in the second term and has a modifying influence on the transformation temperature. In the absence of the second phase, using the approach of Patel and Cohen [18] Eq. (3) becomes $M_s = T_0 + \frac{1}{B}\left[\sigma_0\varepsilon_0/3 + \tau_0\varepsilon_0' - F_c\right]$. Because the product of the shear stress and strain is always positive, it will raise M_s. The axial term, on the other hand, will raise M_s in tension and lower it in compression due to the positive volumetric strain.

The thermodynamic force for the reverse transformation is reduced due to the dissipation of stored elastic strain energy during the forward transformation [12]. The reverse transformation starts at

$$A_s = T_0 + \frac{1}{B}\left[\sum_n \Sigma_{ij}(1-\alpha)\varepsilon_{ij}^n\right.$$
$$\left. + \sum_n (1-\beta)\left(\sigma_{ij}^{\gamma\text{-dist}}\right)^n(1-\alpha)\varepsilon_{ij}^n + F_c\right] \qquad (4)$$

Here elastic strain energy dissipation can be evaluated via a reduction in the transformation strain represented by $\varepsilon_{ij}^{*n} = \varepsilon_{ij}^n(1-\alpha)$ where ε_{ij}^{*n} is the modified transformation strain due to plastic accommodation, i.e. dislocation emission. If $\alpha = 0$, plastic relaxation does not occur; however, if $\alpha > 0$, the transformation strains are reduced. When $\alpha = 1$, the transformation strain is zero and the strain that accumulates is a result of plastic deformation. The emission of dislocations reduces the internal strains of the second phase as well and the $(1-\beta)$ factor represents the relaxation of stress fields at the second phase interface. In addition to reduced contribution from the strain energy terms, immobile dislocations emitted due to the transformation and residual martensite create a frictional resistance to the reverse

transformation that should increase F_c. As mentioned earlier, plastic relaxation is enhanced by the positive large volumetric strain in tension thus the α term should be significant. In fact, we find that the A_s temperature increases by 100 °C in tension for the aforementioned reasons. Note that dislocation and residual martensite stress fields favor the external stress and help the forward transformation causing the M_s temperature for subsequent transformation cycles to increase.

3. Material and experimental results

The chemical composition of the material was measured after single crystal growth as 40 at.%Co, 33.17 at.%Ni and 26.83 at.%Al. An extensive set of differential scanning calorimetry (DSC) experiments were conducted on the samples. The annealing temperatures were held at 1200 °C, 1275 °C and 1350 °C for annealing times varying from 0.5 h to 48 h. The variation of transformation temperatures with the annealing times for the 1275 °C hold temperature is shown in Fig. 2. The thermal hysteresis is of the order of 25 °C and the transformation temperatures increase with increasing annealing time. Based on these results the 1275 °C 3 h heat treatment was chosen as the heat treatment for our subsequent experiments. Optical microscopy (Fig. 3) exposes the γ phase, which does not undergo the martensitic transformation. The γ phase can prevent the reverse transformation hence residual martensite remains. The image reveals a distinct lamellar, eutectic-like $\gamma + \beta$ microstructure.

Stress–strain response was studied at 100 °C, i.e. above the A_f temperature, for tension. Fig. 4 to ensure that recoverable strains were exclusively due to pseudoelasticity. Therefore, residual strains were not recovered upon heating. We note that the transformation stress in

Fig. 3. A typical lamellar, eutectic-like microstructure of Co–Ni–Al displaying the two phases in the parent alloy and the residual martensite. We note that the martensite is confined to the parent phase.
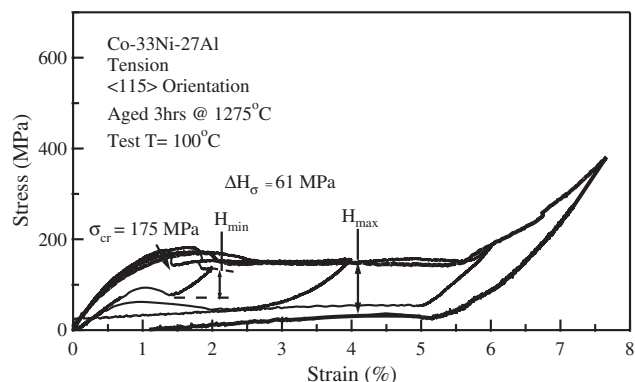
Fig. 4. Stress–strain response of [1 1 5] crystals in tension. The recoverable strain (excluding elastic recovery) is 6%.

this material is of the order of 175 MPa in tension and recoverable strains as high as 6% were achieved. The stress strain curve exhibits the familiar transformation under a constant stress followed by an upward curvature indicative of the conclusion of the transformation. The stress hysteresis changed from $H_{min} = 57$ MPa to $H_{max} = 118$ MPa with increasing strain. The increase in stress hysteresis is 61 MPa.

To gain further insight into tensile strains and thermal hysteresis, a second series of experiments were undertaken under constant stress with temperature cycling Fig. 5. The temperature cycling started with the load applied above A_f, to ensure the specimen was fully austenitic. The external stress was increased incrementally until either the transformation strain saturated or the specimen showed a significant level of unrecoverable (plastic) strain. Specifically, residual strain accumulated for +35 MPa while at +50 MPa complete recovery occurred, residual strain remained again at +60 MPa, and then complete recovery occurred at +70 MPa.

The large hysteresis growth (ΔH_T) in tension between +25 MPa ($H_{min} = 37$ °C) and +70 MPa ($H_{max} = 90$ °C) is 53 °C. Remarkably, the ΔA_s in tension is 100 °C.
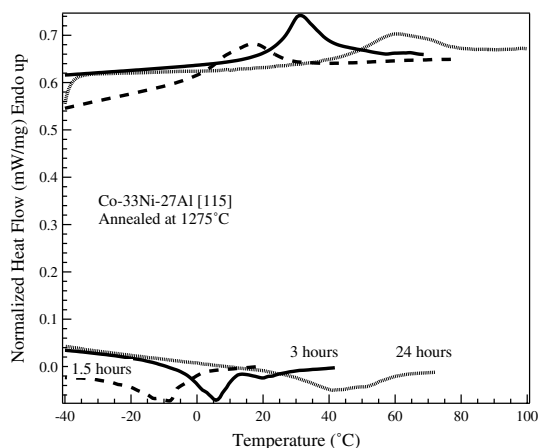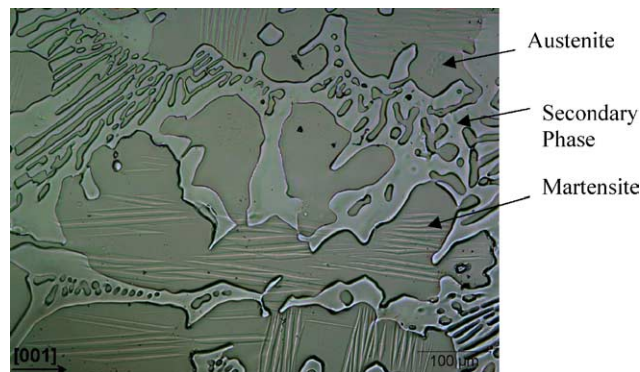

Fig. 2. Differential scanning calorimetry results for annealing at 1275 °C for different times. Note that with increasing annealing times the transformation temperatures are shifted to higher temperatures.
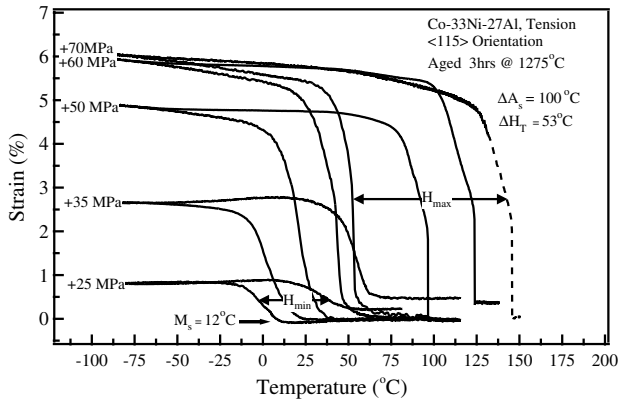
Fig. 5. Strain–temperature response of Co–Ni–Al at different tensile stress levels.

Finally, we note that the maximum stress hysteresis levels observed were on the order of 155 MPa (H_{max} in Fig. 4(b)) compared to the thermal hysteresis levels of 90 °C (H_{max} in Fig. 5(a)). The thermal hysteresis level of 90 °C represents a much higher level of irreversibility than the 155 MPa value confirming the non-equivalence between the isostress and isothermal experiments. The stress dependencies of the hysteresis evolution, transformation temperatures, and strain recovery are indicative of energy dissipation [12] and are elaborated on in the discussion section below.

4. Discussion of results

The experimental results demonstrate the remarkable ability for the [1 1 5] single crystal Co–Ni–Al alloys to undergo large transformation strains in tension. Although the magnitude of the transformation strain in tension for the [1 1 5] orientation is lower than the theoretical levels, it is as high as 6.5% for thermal cycling under constant load. The tensile transformation strain levels are slightly below the theoretical correspondent variant pair (CVP) strains and far below the theoretical CVP plus detwinning strain. This is partly because of plastic relaxation attributed due to the large volumetric strain, the large volume fraction of secondary phase, and the introduction of residual martensite. The lamellar, eutectic-like $\gamma + \beta$ microstructure limits the maximum transformation strain from being attained as it does not undergo phase transformation. The secondary phase contributed to increased ductility in this class of Co–Ni–Al alloys similar to the enhancement of ductility in the B2 NiAl type alloys. Presumably the increased ductility promotes higher transformation strains; however, the results indicate that the microstructure and the volumetric strain prohibit achievement of the theoretical values in tension.

The Co–Ni–Al single crystals in this study exhibited a considerable increase in temperature hysteresis with increasing applied stress in tension (Fig. 5). On the other

hand, the stress hysteresis expanded with increasing applied strain. The magnitude of the transformation hysteresis is much higher in the isostress thermal cycling experiments compared to the isothermal experiments. Such a marked difference in behavior between constant load (isostress) thermal cycling and isothermal stress–strain behavior deserves further study and we now briefly propose a rationale. We first note that stresses applied during thermal cycling are of the order of 2–4 times lower than the critical transformation stress for the pseudoelastic cases. The difference in the temperature and stress hysteresis evolution is rationalized considering contrasting variant interactions in isothermal stress–strain versus isostress thermal cycling at such low stresses. During isothermal stress–strain deformation above A_f the transformation is exclusively stress-induced thus favorably oriented CVPs are nucleated and there is limited CVP interaction. On the other hand, in isostress thermal cycling at low stresses, CVPs oriented favorably to the external stress as well as those oriented to the internal stress exists due to the non-transforming γ phase. Consequently, internal–external stress induced CVP interactions [21] and variant-second phase interactions will be more influential for the low-stress thermal cycling cases. External stress should dominate internal stress fields well above the A_f temperature at the transformation stress hence the influence of the second phase is diminished. Fundamentally, the energy contributions (i.e. stored elastic strain energy and irreversible mechanisms) are significantly different for the two testing conditions producing the observed contrasts in behavior. In the following paragraph, we focus on the noteworthy disparity in temperature hysteresis for temperature cycling under monotonically increasing constant loads.

The growth of hysteresis is attributed to the relaxation of coherency stresses at inter-phase boundaries causing stored elastic strain energy dissipation and dislocation emission. Hamilton et al. [12] discuss the role of matrix strength and that plastic accommodation of the transformation strains is expected to occur more readily in a softer parent phase. In thermal cycling under monotonically increasing load, the corresponding increase in transformation strain produces more severe plastic relaxation of coherent stresses at martensite–austenite interfaces. As a result, the level of stored elastic strain is lowered hence its contribution to the reverse transformation decreases, and the chemical driving force must increase. This requires further heating causing the hysteresis to expand with increased load. The higher CVP strains and localized detwinning in the tension case promote a wide hysteresis in tension.

We now discuss the tensile stress–strain response. The results demonstrate that the stress levels required to induce transformation are as low as 175 MPa at 100 °C in tension. This low transformation stress is a prerequisite to achieve large transformation strains as it ensures that

the stresses do not approach levels that cause slip deformation in the austenite. As mentioned earlier, the predominant growth of external stress induced martensite minimizes energy dissipation due to variant–variant interactions. In a prior study, we found that the critical stress decreased with increased deformation for the polycrystalline material [4]. The present results show that the critical stress levels are quite stable for increasing strain levels, which indicates that the role of irreversiblities (i.e. dislocation generation and residual martensite) is diminished for the stress strain case; otherwise, the critical stress would increase or decrease. The stress hysteresis growth and critical transformation stability in tension indicate that the decreased variant interactions for the pseudoelastic case minimize the influence of dissipative mechanisms.

5. Conclusions

1. The eutectic phase enhances the ductility of the matrix allowing the [1 1 5] oriented single crystals to achieve high transformation strains in tension near 6%. The non-transforming eutectic (secondary) phase, traps a large volume fraction of residual martensite ruling out the realization of the theoretical CVP and detwinning strains in tension. Enhanced plastic accommodation due to the large volume change further suppresses the transformation strains in tension.
2. The thermal and stress hysteresis observed in the experiments, and their respective growth with increasing stress and increasing strain, are drastically different. In the isothermal stress–strain experiments, the transformation proceeds at much higher stress levels compared to the isostress thermal cycling experiments (<50 MPa). For the isostress case, both the internal stress and multiple variant interactions associated with the eutectic-like (secondary) phase play a substantial role. This leads to the remarkable increase in the temperature hysteresis with increasing stress in tension (as much as 53 °C) due to the volumetric strain induced plastic accommodation. In the isothermal experiments, however, the high external stress produces variant coalescence reducing the interaction term (hence the irreversibilities) reflected in the energy formulation.

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