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# ON THE TEMPERATURE DEPENDENCE OF THE SUPERELASTIC STRENGTH AND THE PREDICTION OF THE THEORETICAL UNIAXIAL TRANSFORMATION STRAIN IN NITINOL

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# On the temperature dependence of the superelastic strength and the prediction of the theoretical uniaxial transformation strain in Nitinol

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## Abstract

This paper describes an alternative method for applying the Clausius-Clapeyron equation in a study of the effect of temperature on the superelastic stress in the shape-memory alloy Nitinol—a candidate material for many medical devices, including in particular, endovascular stents. This new analysis will provide some clarification on the controversy regarding estimation of the thermodynamic equilibrium temperature. The theoretical uniaxial transformation strain has been calculated by means of the Clausius-Clapeyron equation. The calculated value of strain, 5.0%, corresponded closely with the experimentally measured value of 4.7%.

## 1. Introduction

Recently, there has been significant interest within the biotechnology community to generate medical products made of Nitinol—the superelastic and shape-memory alloy consisting of ~50 at. % Ni and ~50 at. % Ti (Duerig *et al.* 1996, Pelton *et al.* 1997). In particular, there has been a considerable and growing effort to develop Nitinol endovascular stents (Bramfitt and Hess 1994, Chuter *et al.* 1995, Beyar 1996, Duerig *et al.* 1996, Makkar *et al.* 1996, Parikh *et al.* 1996, Pelton *et al.* 1997). Nitinol stents would offer several advantages over currently manufactured stainless steel stents by exploiting the material's superelastic effect. These benefits include ~8% reversible 'elastic' strain, biased-stiffness (i.e. a difference in elastic modulus on loading vs.

unloading), and compatibility with magneto-resonance imaging as Nitinol is nonmagnetic (Duerig *et al.* 1996). Since such superelasticity involves the alloy's ability to undergo a geometrically reversible stress-induced martensitic phase transformation, stents would be designed to be superelastic at human body temperature (i.e. 37°C), and therefore would require the <u>stress-free</u> martensite to austenite phase transformation to be complete below this temperature.

One of the most important parameters to consider when designing devices with Nitinol is the magnitude of reversible 'elastic' strain. This parameter can be theoretically calculated by applying the Clausius-Clapeyron equation to stress-strain data. However, there has been much dispute in the literature (Warlimont *et al.* 1974, Wayman and Tong 1974, Olson and Cohen 1977, Wayman and Tong 1977, Melton and Mercier 1981) regarding the selection of the thermodynamic equilibrium temperature, $T_{\mathrm{eq}}$, where the chemical free energies of the parent and martensite phases are equal[1]. Specifically, this controversy focuses on whether $T_{\mathrm{eq}}$ is greater than or less than $A_{\mathrm{f}}$, the austenite finish temperature. Furthermore, much attention is spent trying to estimate $T_{\mathrm{eq}}$ in order to apply the Clausius-Clapeyron equation to experimental data; examples of such estimates which were suggested by Melton and Mercier, 1981 and Wayman and Tong, 1977 respectively are

$$T_{eq} = \frac{M_s + A_s}{2} \text{ and } T_{eq} = \frac{M_s + A_f}{2} \quad ,$$

where $M_{\mathrm{s}}$ and $A_{\mathrm{s}}$ are the martensite and austenite start temperatures. Melton and Mercier state that their estimate for $T_{\mathrm{eq}}$ unfortunately results in a large error (e.g. ~61%) between their experimentally measured and calculated enthalpies.

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[1] The previous authors denoted the thermodynamic equilibrium temperature as $T_0$; as this notation is later applied to a different parameter in the current article, the present authors prefer $T_{\mathrm{eq}}$.

The purpose of this paper is to report experimental uniaxial tensile data for the thermoelastic alloy Nitinol, and to describe a new approach to applying the Clausius-Clapeyron equation to analyze such results. Furthermore, this alternative method avoids the previous problems of estimating $T_{\text{eq}}$ by performing a simple integration. In addition, the theoretical transformation strain under uniaxial tension is calculated via the Clausius-Clapeyron equation and has an accuracy of ~6.0% when compared to experimentally measured data.

## 2. EXPERIMENTAL METHODS

The material studied had a composition of 55Ni-45Ti (wt. %). Round bar uniaxial tension samples (gauge length = 25.4 mm; diameter = 6.40 mm) were heat treated in air at 500°C for 35 minutes before rapidly quenching in an ice water bath. The martensite/austenite transformation temperatures were determined using differential scanning calorimetry (DSC). To begin the DSC tests, the sample temperature was held at 100°C. After the samples (~50 mg) reached thermal equilibrium, they were cooled under automated computer control to –150°C, at a scan rate of 10°C/minute. The same scan rate was used on heating, as the sample temperature returned to 100°C. Tensile tests were conducted under displacement control at a rate of 2.5 μm/sec which corresponded to a strain rate of $\sim 2.5 \times 10^{-5}$ /sec for the selected gauge length. The monotonic constitutive behaviour was measured over the temperature range 37°C-120°C; samples were heated in air via infra-red heat lamps or in a warm distilled water bath [minimal corrosion effects were expected with this environment in Nitinol (Rondelli *et al.* 1989)]. The sample temperature was maintained during testing to within ±0.2°C of the target value.

## 3. RESULTS AND DISCUSSION

### 3.1 *Calorimetry*

Calorimetry revealed the presence of three phase transformations, as shown in figure 1. On cooling, the transformation from austenite (B2, CsCl) to the rhombohedral phase (point group: $\bar{3}m$; space group: $P\bar{3}1m$) (Goo and Sinclair 1985), often referred to as 'R-phase', began at approximately 23.1°C ($T = R_s$) and was complete at 11.6°C ($T = R_f$). With further cooling, the martensitic (space group: $P2_1/m$) (Michal and Sinclair 1981) transformation began at –26.9°C ($T = M_s$) and was finished at –54.8°C ($T = M_f$). No further phase changes were observed as the temperature was lowered to –150°C. Upon heating, the temperature ranges for the reverse transformations of the R-phase and martensite overlapped, and hence, only one endothermic peak was observed despite the presence of both transformations (Saburi and Wayman 1979, Goo and Sinclair 1985, Savvinov *et al.* 1985, Hwang and Yang 1992). This peak was associated with the austenite transformation which started at 13.6°C ($T = A_s$) and was finished at 31.3°C ($T = A_f$). The enthalpies for each reaction were -5.328 J/g, -9.014 J/g, and +18.130 J/g for the R-phase, martensite, and austenite transformations, respectively. Over the temperature range $A_f$ to $M_d$, where $M_d$ is defined as the upper limit for the existence of stress-induced martensite, the material is expected to relieve strain-energy by a phase transformation when under a critical load. It must be emphasized that $A_f$ is slightly less than 37°C, indicating that the material should be superelastic at human body temperature; indeed, this expectation was confirmed with tensile tests which below are described.

### 3.2 *Temperature dependence of superelastic strength*

Tensile tests were conducted over the temperature range 37°C to 120°C. In order to verify that the material was superelastic, the residual permanent set, or lack thereof, needed to be measured on a sample loaded to greater than 1% strain. This test was conducted at 37°C, on a sample which was arbitrarily displaced to ~4.5% strain, and then unloaded (figure 2). The alloy displayed linear elastic distortion until the critical stress (~407 MPa) to nucleate martensite in the material was applied (figure 2). The volume fraction of martensite increased along the loading plateau until it was unloaded at ~4.5% strain; next, the stress decreased until ~200 MPa, at which point, the volume fraction of martensite decreased along the lower stress plateau. After complete unloading, there was no detectable permanent strain, and hence, the transformation was superelastic and geometrically reversible. The complete uniaxial constitutive behaviour at 37°C is shown in figure 3. The alloy displayed a loading stiffness of 62 GPa until the critical stress (~407 MPa) to nucleate martensite in the material was applied. The volume fraction of martensite increased along the loading plateau to approximately 4.7% strain, at which point, the transformation was presumed to be nearly complete, and the stress began to increase again with a loading stiffness of 22 GPa. The 0.2% offset plastic-yield point from the second linear elastic region was found to be 1058 MPa at a strain of 8.2%. The strain-to-failure, $\varepsilon_f$, was 21.3% (for a 25.4 mm gauge length). At high enough temperatures (i.e. $T > M_d$), the loading plateau associated with the stress-induced martensitic transformation was not observed; instead, the material remained stable as the austenite phase. A plot of this uniaxial constitutive behaviour at 120°C is shown in figure 4. At this temperature, the material displayed an elastic loading stiffness of 74 GPa. The 0.2% offset plastic-yield strength was found to be 715 MPa. Following yielding, substantial work-hardening was observed, until the sampled failed at $\varepsilon_f = 11.0\%$.

To measure the effect of temperature on the critical stress to induce the martensitic transformation, tensile tests were conducted at intermediate temperatures in the range of 37°C to 120°C. Figure 5 is a plot of the initial yield or superelastic stress as a function of temperature; when a loading plateau was observed these data were characterized by 3 different methods: the peak stress immediately before transformation, the plateau stress, and the 0.2% offset. The superelastic stress was found to increase with temperature until ~80°C; above this temperature, the material did not undergo a stress-induced transformation, and hence, did not display a loading plateau. The temperature of 80°C corresponded to the limit of martensitic deformation, $M_d$. Above 80°C, little variation was observed in the plastic-yield strength of stable austenite. The data at $T < M_d$ are plotted again slightly differently in figure 6. These data have been scaled and normalized by an arbitrary reference stress and temperature, respectively, in order to linearize this region; the results of curve fitting are included in the figure, where the slope of the fit describes the so called 'stress-rate' (Duerig and Zadno 1990).

### 3.3 *Prediction of the transformation strain*

The theoretical transformation strain, $\varepsilon^T$, can be predicted by applying the Clausius-Clapeyron relationship. Previous attempts (Warlimont *et al.* 1974, Melton and Mercier 1981) to utilize this equation have been compromised by problems associated with estimating the value of the thermodynamic equilibrium temperature $T_{eq}$. Indeed, this point has led to considerable controversy in the literature (Wayman and Tong 1974, Olson and Cohen 1977, Wayman and Tong 1977). The present approach alleviates this problem.

Given that the experimental set up of interest is uniaxial (and not multiaxial) tension, the following one-dimensional derivation can be used to accurately describe the thermodynamic system. Consider that, at some critical stress, $\sigma^{\mathrm{T}}$, the parent austenite phase will begin to transform to martensite in order to reduce the strain energy, viz.:

$$g_{\mathrm{A}} = g_{\mathrm{M}} \quad , \tag{1}$$

where $g_{\mathrm{A}}$ and $g_{\mathrm{M}}$ are the Gibbs-free energy per unit volume for the austenite and martensite phases, respectively. At equilibrium,

$$dg_{\mathrm{A}} = dg_{\mathrm{M}} \tag{2}$$

must be valid. By means of the Gibbs-Duhem equation, the partial Gibbs free energies can be expressed in terms of entropy and work, and hence, equation (2) becomes

$$-s_{\mathrm{A}}dT - \varepsilon_{\mathrm{A}}d\sigma^{\mathrm{T}} = -s_{\mathrm{M}}dT - \varepsilon_{\mathrm{M}}d\sigma^{\mathrm{T}} \quad , \tag{3}$$

where $s$ is the entropy per unit volume and $\varepsilon$ is the strain for either the austenite or martensite phase. At constant pressure, however, the relationship between entropy and enthalpy, $h$ (per unit volume), can be used; rearranging the equation in terms of the stress-rate, gives

$$\frac{d\sigma^{\mathrm{T}}}{dT} = \frac{-\Delta s}{\varepsilon^{\mathrm{T}}} = \frac{-\Delta h}{T\varepsilon^{\mathrm{T}}} \quad , \tag{4}$$

where $\varepsilon^{\mathrm{T}}$ is simply the difference between $\varepsilon_{\mathrm{M}}$ and $\varepsilon_{\mathrm{A}}$. This is the Clausius-Clapeyron equation [equation (4)]; however, the pressure and volume terms which traditionally appear in this relationship have been replaced by the conjugate variables stress and strain. For this study, the enthalpy was measured via the DSC tests, and is given in terms of energy/mass, (as opposed to energy/volume). Therefore to maintain consistency of units, equation (4) must be multiplied by the density of Nitinol [e.g. 6.45 g/cm$^3$ (Hodgson and Biermann 1990) for the austenite phase], $\rho_{\mathrm{A}}$, and thus,

$$\frac{d\sigma^{\mathrm{T}}}{dT} = \frac{-\Delta h \rho_{\mathrm{A}}}{T\varepsilon^{\mathrm{T}}} \quad . \tag{5}$$

To linearize the data with respect to temperature, equation (5) has been integrated to give:

$$\left(\sigma^{\mathrm{T}} - \sigma_0\right) = \frac{-\Delta h \rho_{\mathrm{A}}}{\varepsilon^{\mathrm{T}}} \ln\left(\frac{T}{T_0}\right) \ , \tag{6}$$

where $\sigma_0$ and $T_0$ are an arbitrary reference stress and temperature, respectively.

For this analysis, the stress-rate from the plateau-stress data set is chosen to best describe the critical stress for transformation as a function of temperature. Using equation (6), the same data are plotted again in figure 6, to remove the temperature dependence from the slope. The transformation strain can be now be calculated directly by using the values for the slope of the plateau data from figure 6 (2626.27 MPa), the sum of the measured enthalpies for the austenite to R-phase and R-phase to martensite transformations from the DSC results (-14.34 J/g), and the density for NiTi [6.45 g/cm$^3$ (Hodgson and Biermann 1990)]; the value for $\varepsilon^{\mathrm{T}}$ under uniaxial tension is calculated to be 3.5%. This value for $\varepsilon^{\mathrm{T}}$ is slightly less than the limit of the plateau strain, which is approximately 4.7% (figure 3). This discrepancy can be removed however, if the 'ordinary' elastic strain contribution (i.e. equal to $\sigma^{\mathrm{T}}/E$) is considered as well. For a precise calculation, the volume fractions of austenite and martensite at the limit of the plateau must be known; with this information, an effective modulus could be calculated by applying a rule-of-mixtures approach for the two different phases. However, an approximation can be estimated using exclusively the martensite stiffness, as the transformation is nearly complete at the point of interest. Using the unloading stiffness at the end of the plateau, equal to 27.5 GPa (figure 2), the 'ordinary' elastic strain is calculated to be 1.5%. By summing this elastic strain to the calculated transformation strain, this approach predicts a theoretical strain of 5.0% which has an accuracy of ~6% when compared to the experimentally observed value of 4.7%, as shown in figure 3. This constitutes a significant improvement on previous attempts in using the Clausius-Clapeyron equation (Melton and Mercier 1981) where the accuracy was an order of magnitude worse.

## 4. CONCLUSIONS

Based on an experimental study and theoretical analysis of the effect of temperature on the critical stress to cause a martensitic stress-induced phase transformation between 37°C and 120°C in a 55Ni-45Ti (wt. %) Nitinol alloy, the following conclusions can be made:

1. The limit of martensitic deformation, $M_d$, was found to be ~80°C for this material after heat treating at 500°C in air for 35 minutes, followed by a rapid ice water quench. At temperatures between $A_f$ and $M_d$, the material displayed a geometrically reversible stress-induced phase transformation while under uniaxial tension. Above $M_d$, the material remained stable as the austenite phase, and the monotonic constitutive behaviour can simply be described as elasticity followed by work-hardening plasticity.
2. A new approach for predicting the theoretical uniaxial transformation strain using the Clausius-Clapeyron equation has been presented. This approach, which alleviates difficulties in estimating the thermodynamic equilibrium temperature, yields predictions of the total transformation strain to within ~6%. This represents a considerable increase in accuracy compared to previous attempts in applying the Clausius-Clapeyron equation to behavior in thermoelastic materials.

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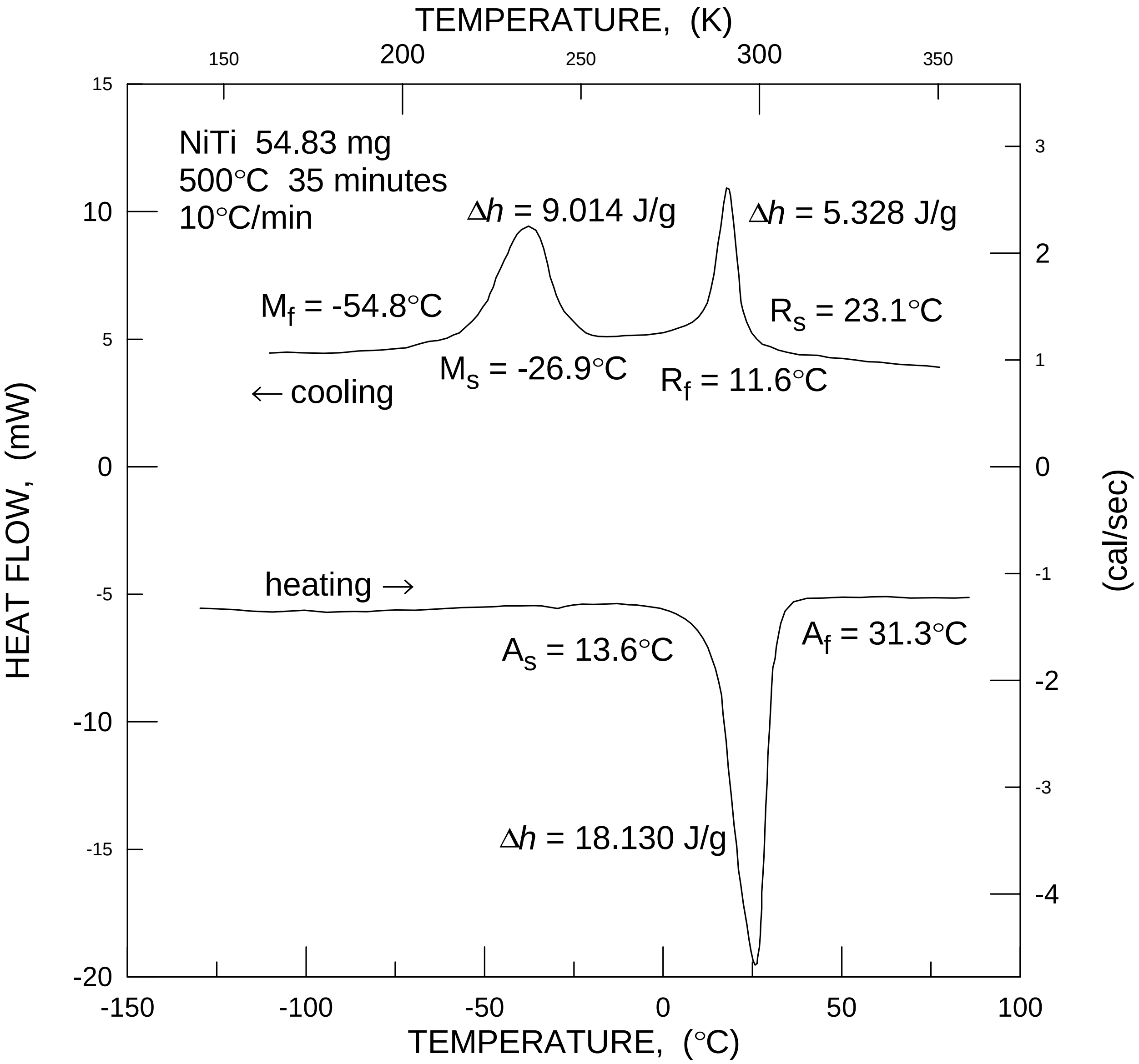

Figure 1: Differential-scanning calorimetry results for NiTi. On cooling, heat was evolved from the sample associated with the transformation from austenite to the rhombohedral phase, often referred to as 'R-phase', which began at 23.1°C and was complete at 11.6°C. With further cooling, the martensitic transformation began at -26.9°C and was finished at -54.8°C. Upon heating, the temperature ranges for the reverse transformations of the R-phase and martensite overlapped, and hence, only one endothermic peak was observed. This peak was associated with the austenite transformation which started at 13.6°C and was finished at 31.3°C.

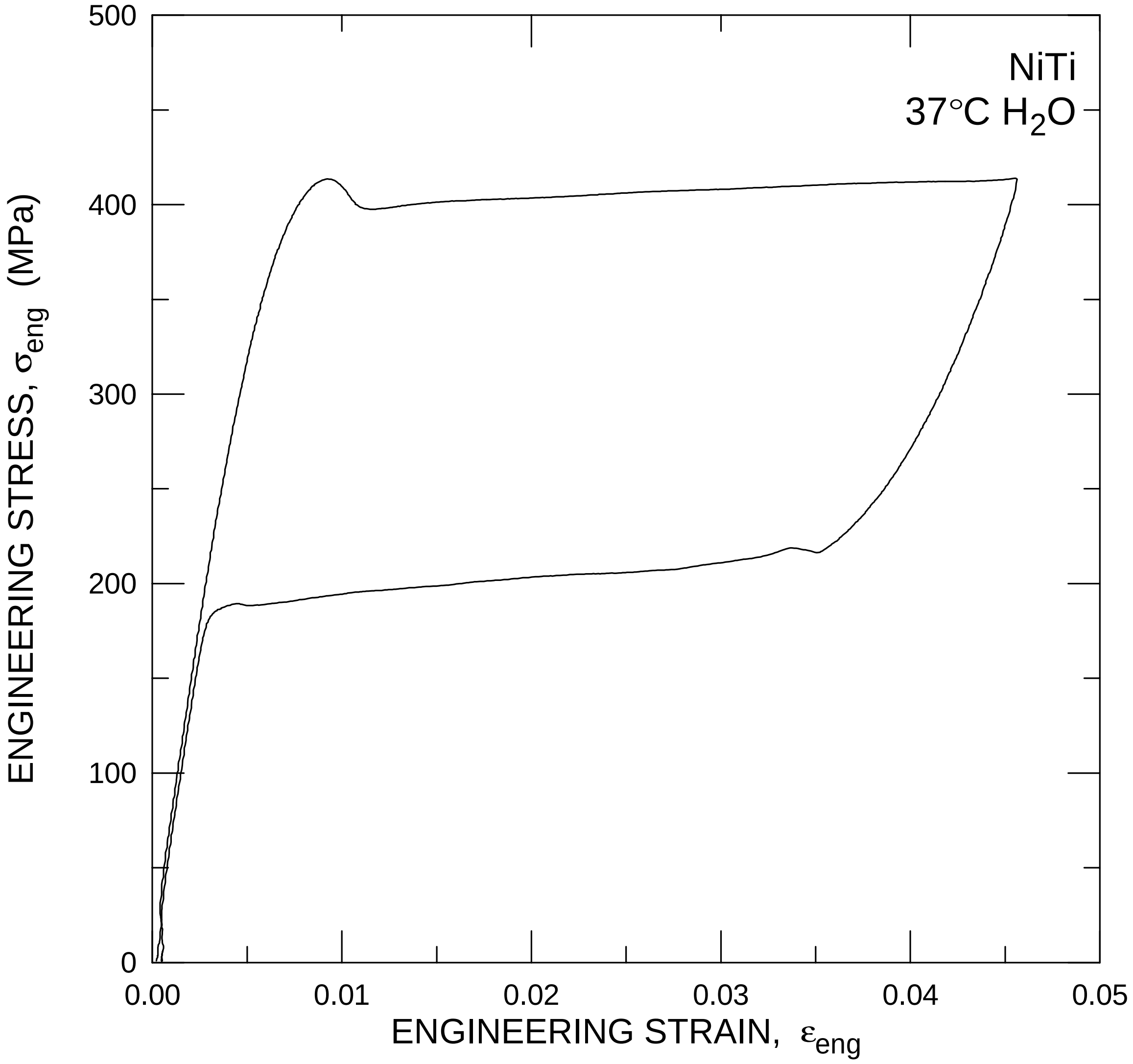

Figure 2: A plot of results which verified that NiTi was superelastic at 37°C, after the material had been heat treated at 500°C for 35 minutes in air followed by an ice water quench. The material displayed linear elastic distortion until the critical stress to nucleate martensite in the material was applied (~407 MPa). The volume fraction of martensite increased along the loading plateau, until the sample was arbitrarily unloaded at ~4.5% strain. At ~200 MPa, the volume fraction of martensite began to decrease along the lower plateau. After complete unloading, there was no detectable permanent strain, and hence, the material was superelastic.

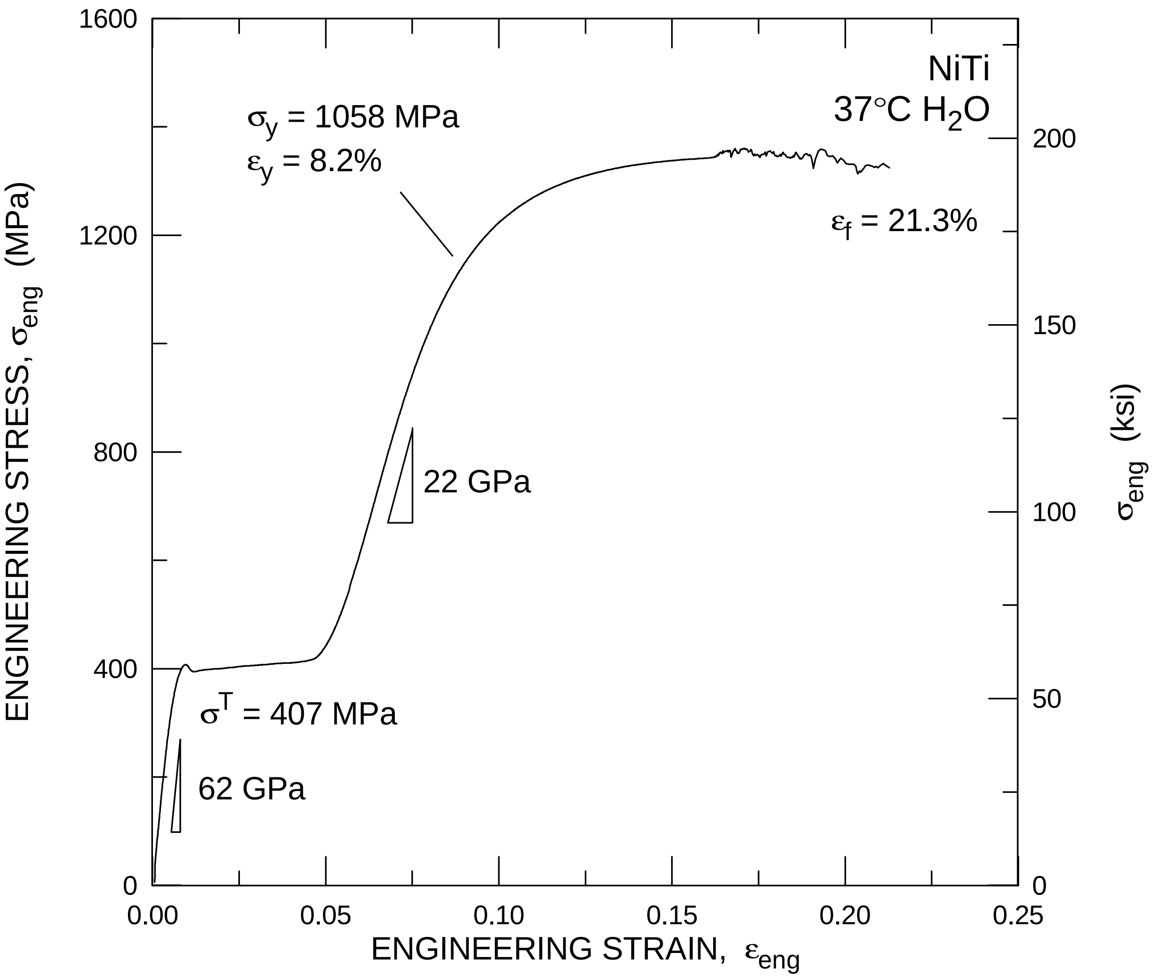

Figure 3: The complete uniaxial constitutive behavior in NiTi at 37°C is shown. The alloy displayed an initial loading stiffness of 62 GPa until the critical stress (~407 MPa) to nucleate martensite in the material was applied. The volume fraction of martensite increased along the loading plateau to approximately 4.7% strain. With further displacement, a new loading stiffness of 22 GPa was observed until general yielding began at 8.2% strain and 1058 MPa. The strain-to-failure was 21.3% for a 25.4 mm gauge length.

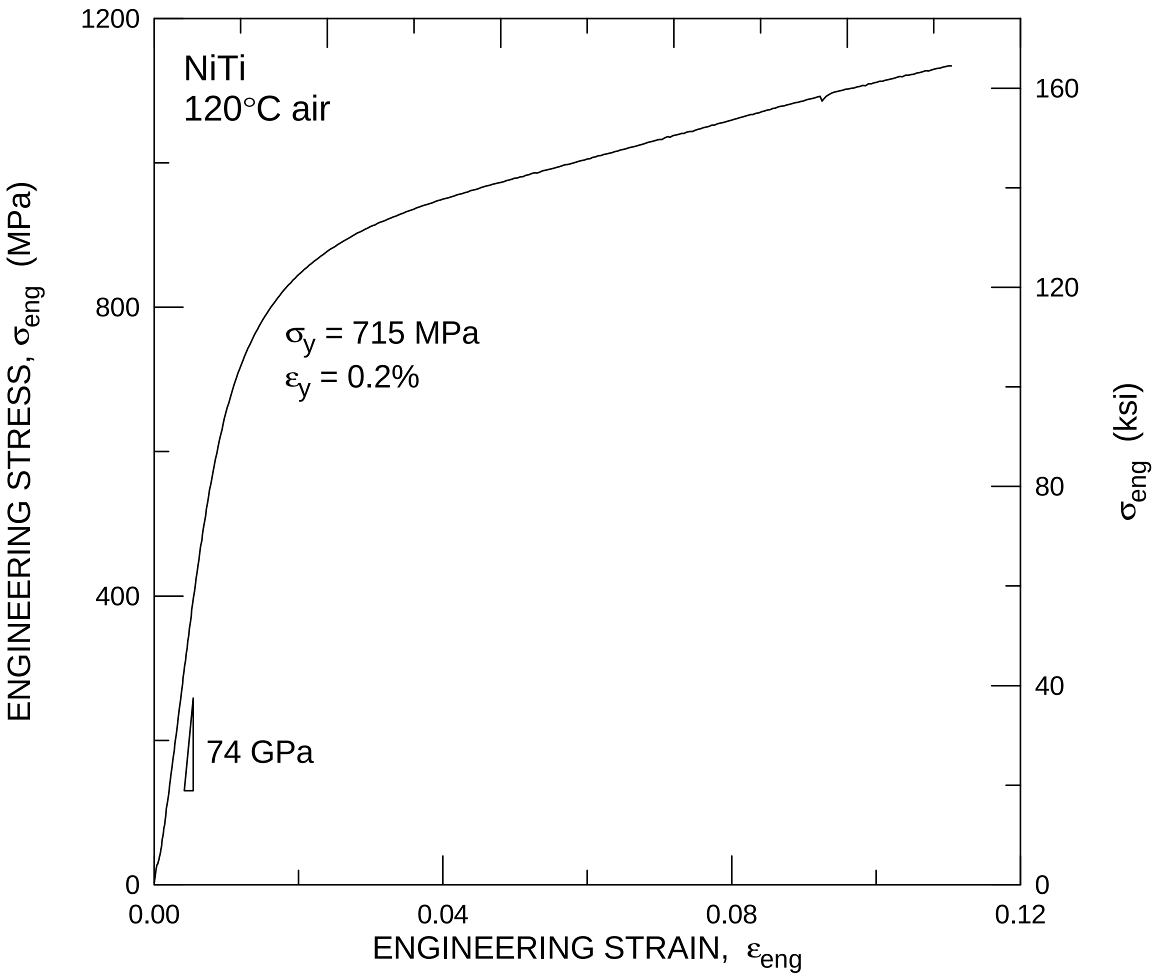

Figure 4: A plot of the uniaxial constitutive behavior in NiTi at 120°C which is greater than $M_d$, 80°C. The material displayed a loading stiffness of 74 GPa. The 0.2% offset yield strength was found to be 715 MPa. The material failed at 11.0% strain with a 25.4 mm gauge length. Note, no superelastic transformation is observed at this temperature.

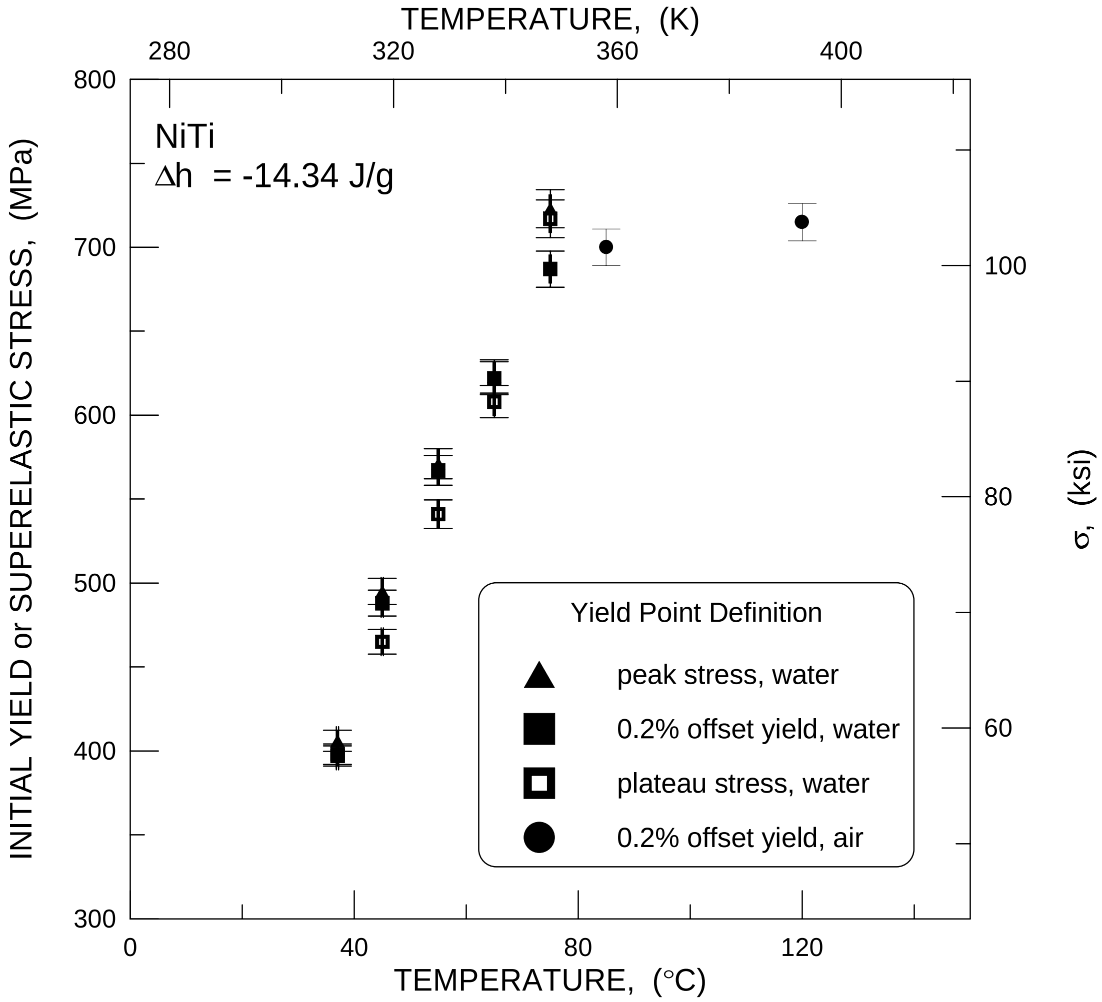

Figure 5: A plot of the effect of temperature on the initial yield or superelastic stress which corresponds to the critical stress to nucleate martensite in the material. As the temperature increases from 37°C, the superelastic stress, $\sigma^T$, increases until ~80°C, which was found to be the temperature limit for the stress-induced martensitic transformation, $M_d$. Below this temperature, data were characterized by the peak stress, the plateau stress, and the 0.2% offset. Above 80°C, a stress-induced martensitic transformation was found to not occur; instead the material displayed simple elasticity followed by work-hardening plasticity. There was little variation observed in the yield strength of stable austenite at $T > M_d$.

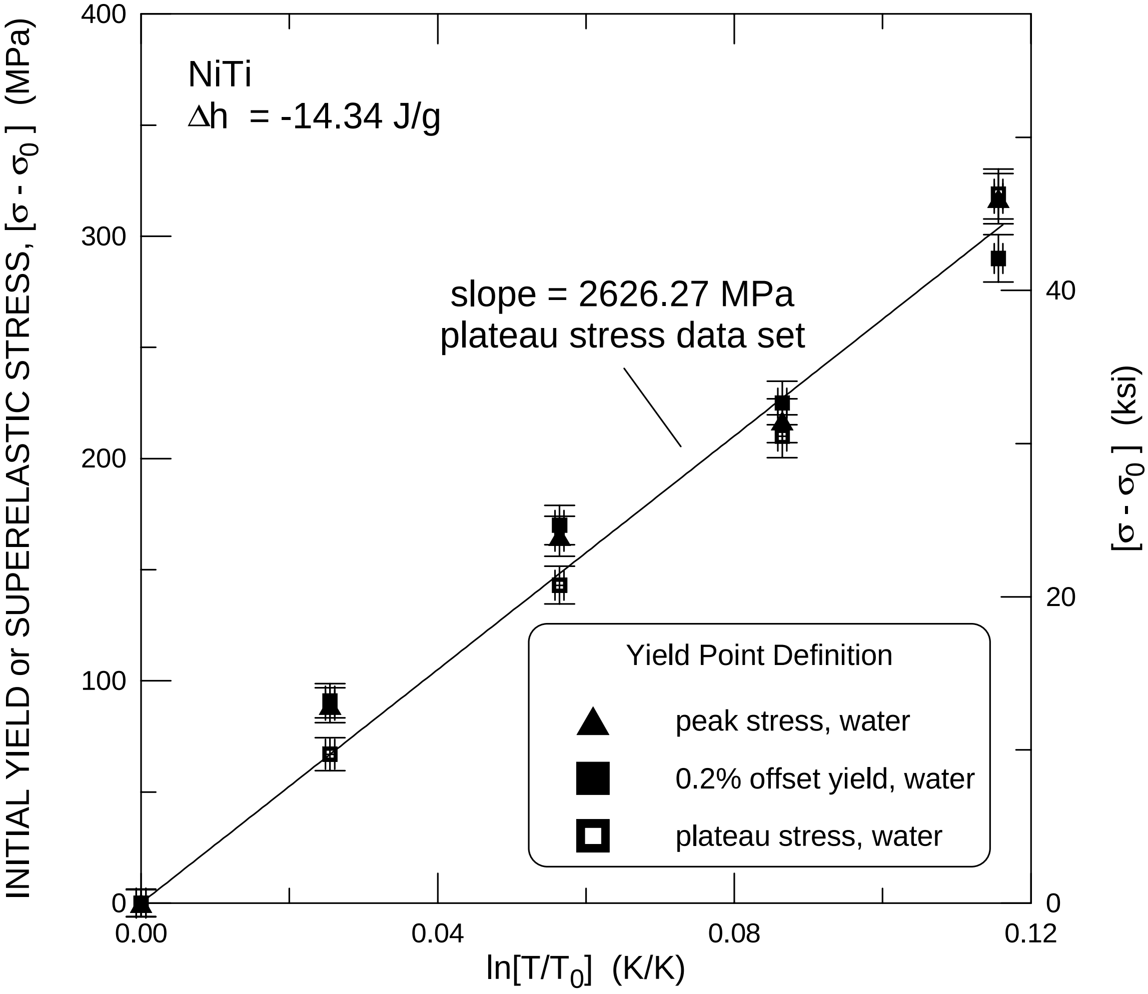

Figure 6: The data at $T < M_d$ shown in figure 5 are replotted; specifically, they have been scaled and normalized by an arbitrary reference stress and temperature, respectively, in order to linearize this region and determine the slope of the data, which describes the 'stress-rate'.