



# Investigation of thermal and stress induced hysteretic curves in CuAl(11.5 wt%) Ni(5.0 wt%) single crystalline shape memory alloy

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## ABSTRACT

Thermoelastic martensitic transformation has been studied in CuAl(11.5 wt%)Ni(5.0 wt%) single crystalline shape memory alloy under constant temperature,  $T$ , as well as under constant uniaxial stress,  $\sigma$ , measuring the relative deformation,  $\epsilon$ , as the function of  $\sigma$  and  $T$ , respectively. From the obtained hysteretic curves the stress/temperature dependence of the martensite and austenite start and finish temperatures/stresses were calculated and discussed in terms of chemical and non chemical energy contributions. The difference between the slopes of the start and finish temperatures versus stress functions and the slope of the equilibrium transformation temperature versus stress is interpreted as the consequence of the  $\sigma$  dependence of the elastic energy term. The transformation strain  $\epsilon^{\text{tr}}$  depends both on  $\sigma$  (at constant  $T$ ) and on  $T$  (at constant  $\sigma$ ) and both functions have the same saturation value, belonging to the stress induced (single) variant martensite structure. It was obtained that the dissipative terms are practically independent of  $\sigma$  and  $T$ , and have higher values for the  $\epsilon \sim T$  than for the  $\epsilon \sim \sigma$  loops.

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## 1. Introduction

Shape memory alloys (SMA) have important technological applications as functional smart materials (see e.g. [1–4]). Especially two alloy families have been commonly used for mass industrial applications, the Ti–Ni and the Cu–Zn–Al alloys [1–3,5,6]. Furthermore, Cu–Al–Ni alloys are being considered for possible use at higher temperatures [4]. These applications imply a deep knowledge of the characteristics of the thermoelastic martensitic transformation, which provides the basis mechanism for shape memory behavior. Thus deeper understanding of the elastic and dissipative energy contributions to the transformation can lead to improved control of the shape memory function [7,8].

In this work, the characteristics of the thermoelastic martensitic transformation have been studied in CuAl(11.5 wt%)Ni(5.0 wt%) single crystalline shape memory alloy under constant temperature,  $T$ , as well as under constant uniaxial stress,  $\sigma$ , measuring the relative deformation as the function of  $\sigma$  and  $T$ , respectively. From the obtained hysteretic curves the stress/temperature dependence of the martensite and austenite start and finish temperatures/stresses as well as of the dissipative and elastic energy terms are calculated on the basis of the model published in [8–11]. Furthermore, the difference between the slopes of start and finish temperatures versus

stress functions and the slope of the equilibrium transformation temperature versus stress is analyzed and interpreted as the consequence of the  $\sigma$  dependence of the elastic term. It is also shown that the transformation strain, as determined from the  $\sigma$ – $\epsilon$  hysteretic loops (at fixed temperatures) has temperature dependence too. We discuss the temperature and stress dependence of  $\epsilon^{\text{tr}}$  via the dependence on the volume fraction of the stress induced (single) variant martensite structure,  $\eta = V_M \sigma / V_M$ , ( $V_M = V_{MT} + V_M \sigma$ , and  $V_{MT}$  and  $V_M \sigma$  denotes the volume of the thermally as well as the stress induced martensite variants, respectively; and the total transformed martensite volume fraction is  $\xi = V_M / V$ , with  $V = V_M + V_A$ ).

## 2. Experimental

Thermally and stress induced martensitic transformations were investigated under constant uniaxial stresses and at constant temperatures, respectively, in CuAl(11.5 wt%)Ni(5.0 wt%) single crystalline samples. The samples were cut from a rod by a simple electro discharge machine and the final dimensions were: 41 mm in length and 0.45 and 0.59 mm<sup>2</sup> in square cross section, respectively. The orientation was [110]<sub>A</sub>. The stress-strain as well as the strain-temperature curves were obtained by a tensile machine (Chatillon TCD225) applying an external heating system in which thermal resistance was used for heating. The heating/cooling rate was approximately  $8 \pm 1 \text{ K min}^{-1}$ . The thermal as well as the stress induced hysteretic loops were determined between 0 and 178 MPa

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(at 10 fixed stress levels) as well as between 373 K and 423 K (at 8 fix temperatures), respectively.

The entropy of transformation was estimated from the measured differential scanning calorimeter runs (DSC Perkin–Elmer DSC-7) at zero uniaxial stress with 2 K/min heating and cooling rate, according to the relations [12]

$$\Delta S^{\downarrow} = \int_{M_s}^{M_f} \frac{dQ^{\downarrow}}{T} \equiv -\Delta S^{\uparrow} = \int_{A_s}^{A_f} \frac{dQ^{\uparrow}}{T}. \quad (1)$$

Here  $Q$  denotes the heat of the transformation and the up and down arrows correspond to the cooling and heating process, respectively. Note that (1) is strictly valid only if the heat capacity difference between the parent and the product phase is zero. Since the difference of absolute values of entropy changes estimated was within the experimental error this approximation was used.

It is well-known that Cu-based shape memory alloys show thermoelastic transformations into various martensitic phases, depending on the chemical composition, temperature and applied stress and its orientation relative to the single crystal axis [13–16]. However, in our alloy, in the temperature and stress range investigated, only the transformation from the high temperature cubic  $\beta$  phase to the  $\beta'$  (18R) phase takes place [13,14].

### 3. Results

Fig. 1 shows the DSC curves measured. The value of the entropy change was calculated from (1) and its magnitude is negative for  $A \rightarrow M$  and positive for  $M \rightarrow A$ :  $\Delta S^{\downarrow}/V \equiv \Delta s/V = -1.58 \times 10^{-5} \text{ J/Km}^3$ , or  $\Delta s = -1.26 \text{ J/K mol}$ . The molar volume of our sample is  $V = 7.9 \times 10^{-6} \text{ m}^3/\text{mol}$ . Note that this value of the entropy is in a good agreement with those obtained for  $\beta$  to  $\beta'$  transformation in alloys of similar composition [14].

Fig. 2a shows the deformation–temperature hysteretic loops at different constant uniaxial stress levels. It can be seen that at low stresses the total  $\epsilon$  belonging to the transformation, i.e.  $\epsilon^{\text{tr}}$ , is small and there is a sudden increase between 15 and 30 MPa, as it is illustrated in Fig. 2b too. It is worth noting that in a more recent conference proceedings [17] we published an analysis of our results obtained for  $\beta$  to  $\gamma'$  [8] as well as for  $\beta$  to  $\beta'$  transformation (which is described here). However, there we have concentrated on a comparative analysis of the  $\epsilon^{\text{tr}}(\sigma)$  (and  $\epsilon^{\text{tr}}(T)$ ) curves, as well as the effect of stress dependence of it on the slope of the equilibrium transformation temperature versus stress functions. Furthermore it was also analyzed how the stress dependence of  $\epsilon^{\text{tr}}$  is reflected in

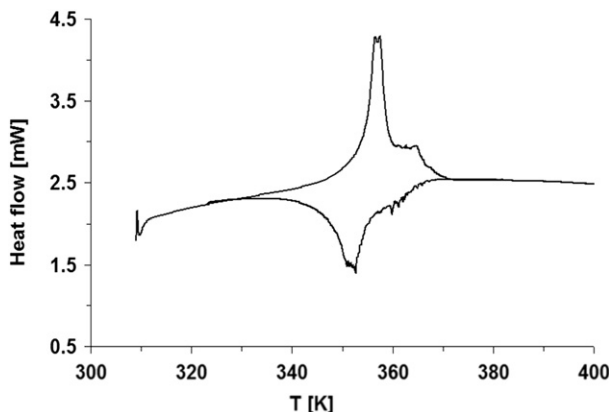


Fig. 1. DSC curve measured at zero stress.

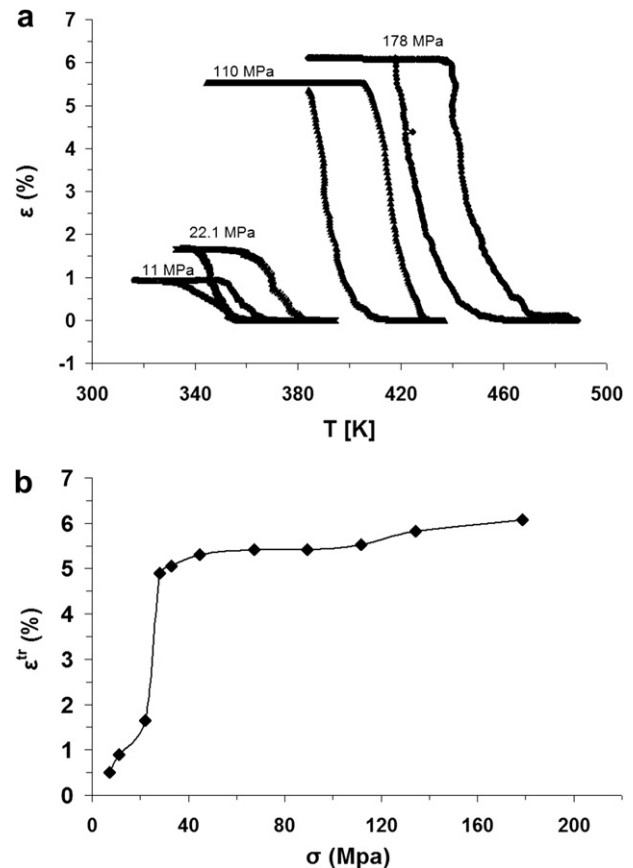


Fig. 2. a) Thermal hysteretic loops ( $\epsilon$  versus  $T$  curves) at four different uniaxial stress levels, b) Transformation strain as function of stress ( $\epsilon^{\text{tr}}$  is the maximal value of  $\epsilon$ ; in Fig. 2a; see also Fig. 3 in [17]).

the dissipative energy contributions for both types of transformations. The details of the results for  $\beta$  to  $\beta'$  transformation (DSC measurements,  $\epsilon$ – $T$  and  $\epsilon$ – $\sigma$  hysteretic loops and the extended analysis of data obtained) are presented here and we mark those figures which already were included in [17].

Fig. 3a shows the  $\epsilon$ – $\sigma$  hysteretic loops measured at different temperatures. Fig. 3b shows the transformation strain as function of temperature: they were calculated from the  $\epsilon$ – $\sigma$  loops. It can be seen that, as it is expected, the maximal value is about the same as on Fig. 2b. From Figs. 2a and 3a the values of the start and finish temperatures and stresses were determined as points where the hysteretic curve leaves as well as returns to the linear lines fitted to the pure phases. Figs. 4 and 5 shows the stress and the temperature dependence of the start and finish temperatures and stresses, respectively.

In order to carry out the analysis on the stress and temperature dependence of the start and finish quantities as well as of the elastic and dissipative energy terms [8,9], the vertical axes of the hysteretic curves were normalized, giving the transformed fraction of martensite phase,  $\xi$ .

### 4. Discussion

#### 4.1. Relations used in the analysis of data

It has been recently discussed in [11] that in the austenite to martensite transformation of shape memory alloys the transformation strain,  $\epsilon^{\text{tr}}$ , usually has definite field dependence while the change in the entropy or volume can be considered constant. Under

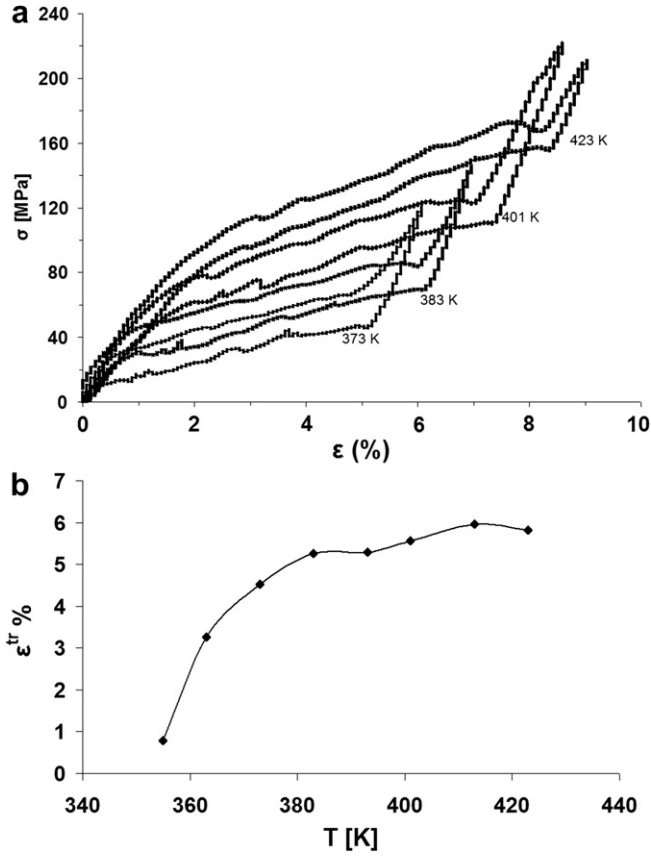


Fig. 3. a)  $\sigma$  versus  $\varepsilon$  at four different temperatures, (b) Transformation strain as function of temperature (red out from curves like those in Fig. 3a; see also Fig. 5 in [17]).

uniaxial loading the field dependence of  $\varepsilon^{\text{tr}}$  is related to the change of the martensite variant distribution with increasing field parameter. For the description of this, the volume fraction of the stress induced (single) variant martensite structure,  $\eta$ , was used.

Furthermore, on the basis of a simple model for the interpretation of the hysteretic loops, in terms of chemical, elastic and dissipative energy contributions [9], it was also shown in [11] that the start and finish temperatures can be given as

$$\begin{aligned} M_s(\sigma) &= T_0(\sigma) - [d_0 + e_0]/[-\Delta S] \\ M_f(\sigma) &= T_0(\sigma) - [d_1 + e_1]/[-\Delta S] \\ A_f(\sigma) &= T_0(\sigma) + [d_0 + e_0]/[-\Delta S] \\ A_s(\sigma) &= T_0(\sigma) + [d_1 + e_1]/[-\Delta S], \end{aligned} \quad (2)$$

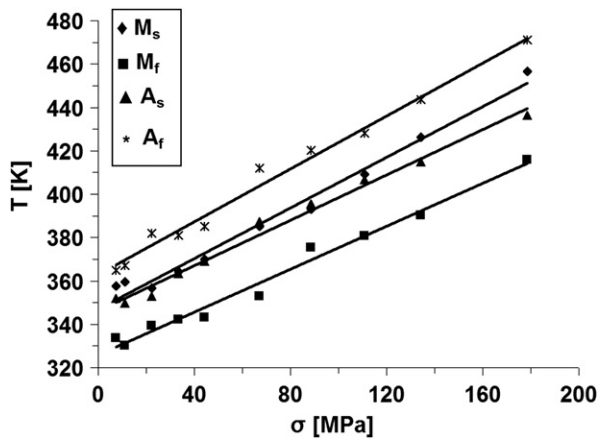


Fig. 4. Start and finish temperatures as the function of stress.

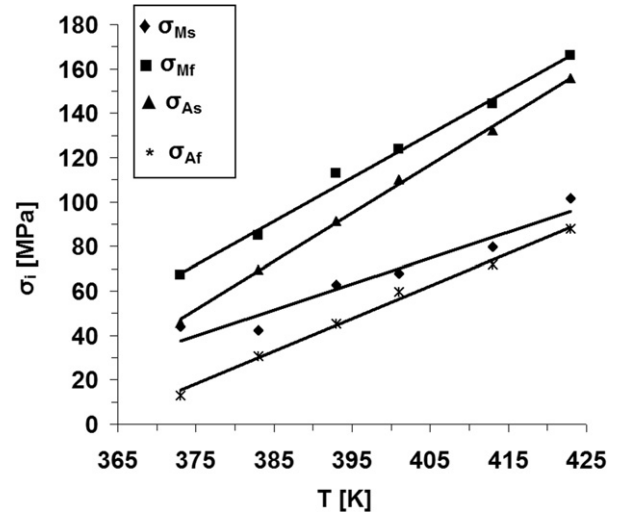


Fig. 5. Start and finish stresses as the function of temperature.

as well as for the start and finish stresses (e.g.  $\sigma_{Ms}(T)$  denotes the stress at which the martensite starts to form at temperature  $T$ ) one has:

$$\begin{aligned} \sigma_{Ms}(T) &= \sigma_o(T) - [d_0 + e_0] [-V\varepsilon^{\text{tr}}] \\ \sigma_{Mf}(T) &= \sigma_o(T) - [d_1 + e_1] [-V\varepsilon^{\text{tr}}] \\ \sigma_{Af}(T) &= \sigma_o(T) + [d_0 + e_0] [-V\varepsilon^{\text{tr}}] \\ \sigma_{As}(T) &= \sigma_o(T) + [d_1 + e_1] [-V\varepsilon^{\text{tr}}]. \end{aligned} \quad (3)$$

Here the quantities on the left hand side have their usual meanings,  $d_0, d_1, e_0, e_1$  denote the derivatives of the changes of the dissipative and elastic energy by the transformed martensite volume fraction,  $\xi$ , at  $\xi = 0$  (martensite start point) and at  $\xi = 1$  (martensite finish), respectively. In writing (2) and (3) the usual assumption in shape memory alloys, namely that for the  $d_i$  and  $e_i$  parameters the  $e_i = e_i \downarrow = -e_i \uparrow$  and  $d_0 = d_0 \downarrow = d_0 \uparrow, i = 0, 1$ , relations hold, was assumed.  $T_0(\sigma)$  and  $\sigma_o(T)$  are the stress and temperature dependent equilibrium transformation temperature and stress, respectively and are given by

$$T_0(\sigma) = T_0(0) - (1/\Delta S)\sigma V\varepsilon^{\text{tr}} \quad (4)$$

and

$$\sigma_o(T) = -(\Delta S/V\varepsilon^{\text{tr}})[T - T_0(0)]. \quad (5)$$

Relations (4) and (5) are the (integral) forms of the Clausius–Clapeyron relation. Note that they are linear function of  $\sigma$  or  $T$  only if  $\varepsilon^{\text{tr}}$  is constant.

In this paper we will consider that the stress and/or temperature dependence of  $\varepsilon^{\text{tr}}$  can be expressed via the  $\eta$  dependence i.e.  $\varepsilon^{\text{tr}}(\eta)$  [11]:

$$\varepsilon^{\text{tr}} = \varepsilon_T + (\varepsilon_\sigma - \varepsilon_T)\eta, \quad (6)$$

where  $\varepsilon_T$  and  $\varepsilon_\sigma$  are the transformation strains when fully thermally induced multi variant structure forms ( $\eta = 0$ ), as well as when the martensite consists of a fully ordered array of stress preferred variants (single variant state,  $\eta = 1$ ), respectively. This is plausible, because according to [11]  $\eta$  (and thus  $\varepsilon^{\text{tr}}$ ) is not constant but can depend on the  $T$  and  $\sigma$  variables. Indeed, it can be very small or even close to zero for the formation of the thermally induced (randomly oriented) martensite variants (usually there is a very small resultant (remanent) strain in single crystalline samples). On the other hand during the formation of stress induced martensite a single variant structure can form ( $\eta = 1$ ) i.e.  $\varepsilon^{\text{tr}} = \varepsilon_\sigma$ . Accordingly in

relations (2)–(5)  $\varepsilon^{\text{tr}}$  should always be taken at that  $\eta$  value which is relevant for the given values of the  $T$  and  $\sigma$  variables.

It is also worth mentioning that there exists a direct relationship between  $T_0(0)$  and  $\sigma_0(0)$  [11]:

$$\sigma_0(0) = \frac{T_0(0)\Delta s}{V\varepsilon^{\text{tr}}(\sigma_0, T=0)} = \frac{T_0(0)\Delta s}{V\varepsilon_0^{\text{tr}}}, \quad (7)$$

here  $\varepsilon^{\text{tr}}$ , plausibly should be taken at the equilibrium transformation stress and zero temperature, i.e. it is a constant and will be denoted by  $\varepsilon_0^{\text{tr}}$  here.

Finally, it was shown in [9] that a local equilibrium model, based on the thermoelastic balance requiring that the derivative of the change of the Gibbs free energy by the martensite volume fraction,  $\xi$ , should be equal to zero, gives the following relations [11]

$$\begin{aligned} T\downarrow(\xi) &= T_0(\sigma) - [d\downarrow(\xi) + e\downarrow(\xi)]/[-\Delta s] \\ T\uparrow(\xi) &= T_0(\sigma) + [d\downarrow(\xi) + e\uparrow(\xi)]/[-\Delta s], \end{aligned} \quad (8)$$

where again the up and down arrows correspond to the cooling and heating process, respectively. In fact the inverses of these functions (i.e. the  $\xi(T\downarrow)$  and  $\xi(T\uparrow)$  curves) are the lower and upper parts of the normalized  $\varepsilon$ – $T$  hysteretic loops, respectively. Thus, making the usual assumptions  $e(\xi) = e(\xi)\downarrow = -e(\xi)\uparrow$  and  $d(\xi) = d(\xi)\downarrow = d(\xi)\uparrow$  and taking the difference and the sum of  $T\downarrow(\xi)$  and  $T\uparrow(\xi)$ , the  $e$  and  $d$  quantities can be calculated as the function of  $\xi$  at different  $\sigma$  levels. (Note that the  $e(\xi)$  function can be calculated irrespective of the  $T_0(\sigma)\Delta s$  constant value [9,11] if  $T_0(0)$  is not known.)

## 4.2. Analysis of experimental data

### 4.2.1. Results from thermal hysteretic loops

First let us investigate, whether the commonly used assumption in the literature (see e.g. [6,7,18]) that the slopes of the start and finish temperatures and the slope of the  $T_0(\sigma)$  are approximately the same or not. From the relations, presented in Sec. 4.1, it is clear that i) strictly even the linear  $\sigma$  dependence of  $T_0$  is not fulfilled in general (see Fig. 2b which illustrates that  $\varepsilon^{\text{tr}}$  is not constant), ii) the  $\sigma$  dependence of the elastic and dissipative terms ( $e_i$ ,  $d_i$ ,  $i = 0,1$ ) as compared to the  $T_0(\sigma)$  function, can also give a contribution to the stress dependence of the start and finish temperatures (see relations (2)). Thus we plotted the  $T_0(\sigma) - T_0(0)$  values versus  $\sigma$  in Fig. 6, calculated from (4) using the measured  $\Delta s/V$  value and the  $\varepsilon^{\text{tr}}(\sigma)$  curve (Fig. 2b). It can be seen that this function can be approximated by a straight line, neglecting the small deviations in the interval between 0 and 40 MPa. In fact this slight S-shape part up to 40 MPa is the consequence of the stress dependence of  $\varepsilon^{\text{tr}}$  (see the insert in Fig. 6). The straight line fitted in the whole stress range, gives the slope  $0.39 \pm 0.05$  K/MPa. At the same time the slopes of  $M_s$  and  $A_f$  as well as  $M_f$  and  $A_s$  (see Fig. 4) are practically the same: 0.59 as well as 0.50 K/MPa, respectively. Thus these differ from the one obtained for the slope of  $T_0(\sigma)$ .

We can analyze whether this difference comes from the stress dependence of  $d_i$  or  $e_i$  parameters or from both. Fig. 7 shows the stress dependence of the  $d_0$  and  $d_1$  quantities, calculated from the differences of the  $A_f(\sigma)$  and  $M_s(\sigma)$  as well as of the  $A_s(\sigma)$  and  $M_f(\sigma)$ , respectively. It can be seen that, within the scatter of the measured points they are independent of the stress, and both has an average value of about  $12 \pm 3$  J/mol. On the other hand the  $e_0$  and  $e_1$  parameters have a linear stress dependence, as it is shown in Fig. 8. The vertical axis of this figure shows the  $T_0(0)\Delta s + e_0$  or the  $T_0(0)\Delta s + e_1$  quantities calculated from the sums of  $M_s(\sigma) + A_f(\sigma)$  and  $M_f(\sigma) + A_s(\sigma)$ , respectively with the help of the quantities  $\sigma V\varepsilon^{\text{tr}}(\sigma)$  (shown already on Fig. 6). Note that since the  $T_0(0)\Delta s$  quantity is

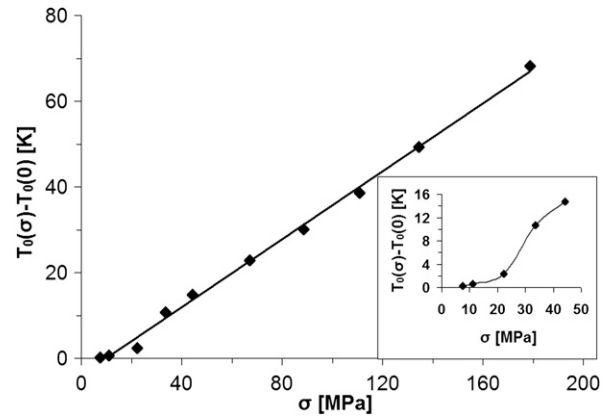


Fig. 6. Calculated stress dependence of the equilibrium transformation temperature,  $T_0$ . (See also Fig. 4 in [17]; note that due to a calculation error in the entropy by a factor of 2.21 in [17], the vertical axis is re-scaled here).

negative ( $\Delta s < 0$ ) and thus from the fact that the values on the vertical axis are negative one can conclude that  $e_0(0) < |T_0(0)\Delta s|$ . The slopes of these curves are  $-0.25$  and  $-0.14$  J/mol MPa, respectively, or dividing it by  $\Delta s$  we have the contribution of the elastic energy contributions to the slopes of the start and finish temperatures (see eq.(3)):  $\partial(e_0/\Delta s)\partial\sigma = 0.20$  K/MPa and  $\partial(e_1/\Delta s)\partial\sigma = 0.11$  K/MPa, respectively. Taking into account that the errors in the estimation of slopes are about  $\pm 0.05$  K/MPa, it can be concluded that the difference between the slopes of the  $T_0(\sigma)$  and  $M_s(\sigma)$  or  $A_s(\sigma)$  is caused by the stress dependence of the elastic energy contributions.

### 4.2.2. Results obtained from $\sigma$ – $\varepsilon$ hysteretic loops

For the analysis of the temperature dependence of  $\sigma_0$ , unfortunately we can not apply a similar procedure as for the stress dependence of  $T_0$ , because we do not know the value of  $T_0(0)$  (see also eq. (5)), where  $\varepsilon^{\text{tr}}$  is temperature dependent as it was shown in Fig. 3b). Nevertheless, the slopes of the straight lines fitted to the start and finish stresses versus temperature functions (Fig. 5) are  $\partial\sigma_{M_s}/\partial T = 1.60$  MPa/K,  $\partial\sigma_{M_f}/\partial T = 1.96$  MPa/K,  $\partial\sigma_{A_f}/\partial T = 1.54$  MPa/K, and  $\partial\sigma_{A_s}/\partial T = 2.17$  MPa/K. Furthermore the slopes of the  $d_i(T)$  and  $e_i(T)$  functions, shown in Fig. 9 as well as 10 and calculated from the differences and sums of the  $\sigma_{A_f}(T)$  and  $\sigma_{M_s}(T)$  as well as  $\sigma_{A_s}(T)$  and  $\sigma_{M_f}(T)$  curves (see Fig. 5), and using the  $\varepsilon^{\text{tr}}(T)$  values given in Fig. 3b, were also determined. For instance in the case of the elastic terms one can write, using relations (3), (5) and (7)

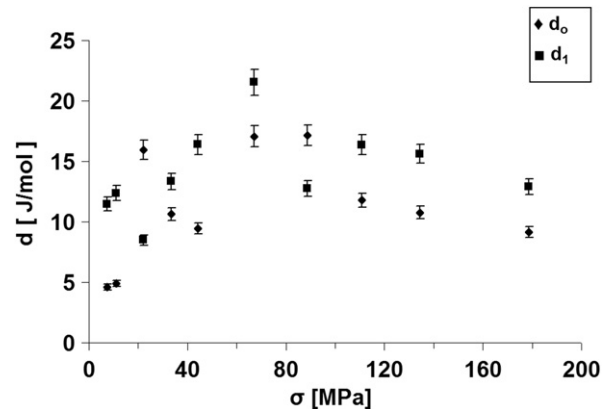


Fig. 7. Stress dependence of the dissipative terms (see also Fig. 7 in [17] with recalculated vertical axis, as mentioned at Fig. 6).



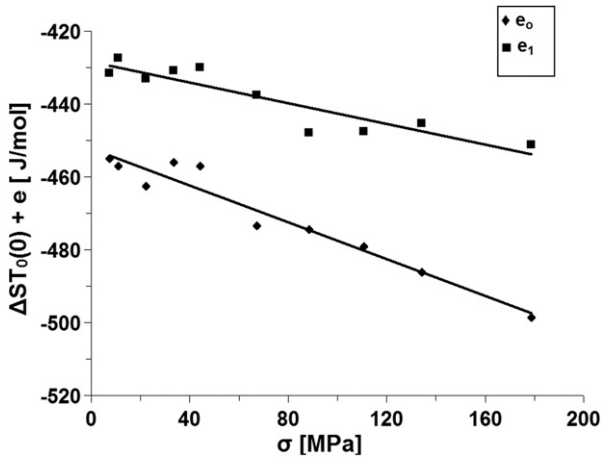


Fig. 8. Stress dependence of the elastic energy terms.

$$\begin{aligned}
 V\varepsilon^{\text{tr}}(T) \frac{[\sigma_{M_s}(T) + \sigma_{A_f}(T)]}{2} + T\Delta S &= V\varepsilon^{\text{tr}}(T)\sigma_0(T) + T\Delta S + e_0(T) \\
 &= T_0(0)\Delta S + e_0(T) \\
 &= \sigma_0(0)V\varepsilon_0^{\text{tr}} + e_0(T),
 \end{aligned}
 \quad (9)$$

A similar relation holds for  $e_1$ . On the left hand side of (9) all the quantities (and their temperature dependence) are known. It can be seen from Fig. 9 that  $d_0(T)$  and  $d_1(T)$  are constant within the experimental errors, and their average value (about  $4.0 \pm 1.5$  J/mol) is lower than the values of  $d_0(\sigma)$  and  $d_1(\sigma)$  shown on Fig. 7. On the other hand  $e_0(T)$  and  $e_1(T)$  are temperature dependent with slopes  $-0.55$  J/mol K and  $-0.18$  J/mol K, respectively (Fig. 10).

#### 4.2.3. Self-consistency of our analysis

The following facts confirm the self consistency of the analysis carried out above.

In both sets of investigations (thermally and stress induced transformations) we have observed that the transformation strain depends on the field parameter (Figs. 2b and 3b), but both have the same saturation value.

This can be interpreted by the increase of the fraction of the stress induced (single) martensite variant structure,  $\eta$ , according to relation (6), from which e.g. an S-shape  $\eta(\sigma)$  function follows.

The difference of the slopes of the linear stress dependence of the start and finish temperatures as well as the slope of the  $T_0$  temperature corresponds to the contribution from the stress

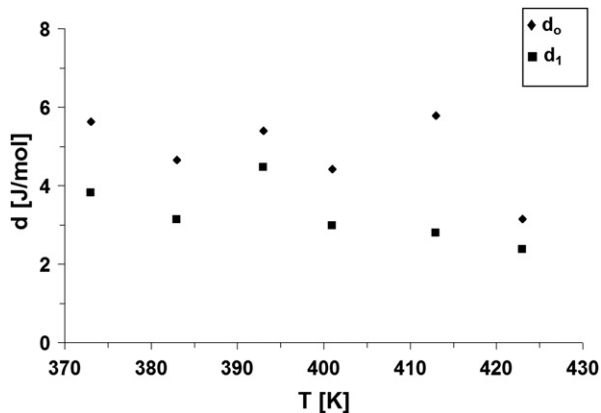


Fig. 9. Temperature dependence of the  $d_i$  quantities ( $i = 0,1$ ).

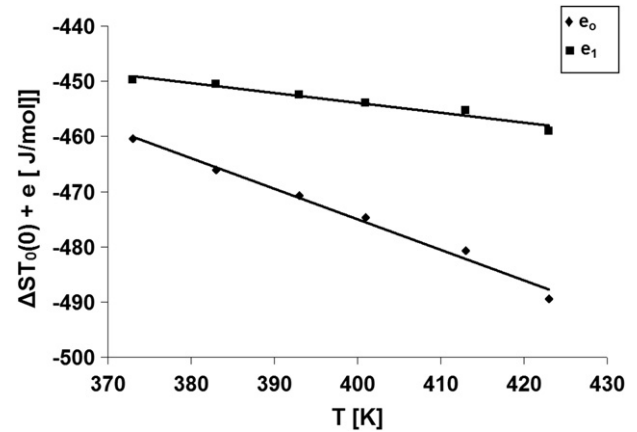


Fig. 10. Temperature dependence of the  $T_0\Delta S + e_i$  quantities ( $i = 0,1$ ).

dependence of the elastic energy terms (the dissipative terms are practically independent of  $\sigma$ ).

The values obtained for the  $d_0$  and  $d_1$  quantities have almost the same values in both sets, but their value is lower for the  $\varepsilon$ – $\sigma$  loops by a factor of 3. It is worth mentioning that most probably both  $d_i(\sigma)$  and  $d_i(T)$  ( $i = 0,1$ ) functions are not constant but the resolution of their dependence on  $\sigma$  and  $T$ , respectively, due to their small values and the experimental errors, is not possible from our data. Nevertheless, Fig. 7 (and Fig. 12 showing 2D versus  $\sigma$ ) suggest that the  $d_i(\sigma)$  functions could have a maximum at about 60 MPa, while at  $\sigma = 0$  MPa as well as at  $\sigma = 178$  MPa its average value is about 6–7 J/mol, which is close to 4 J/mol obtained from the  $d_i(T)$  functions. Furthermore, since at higher temperatures higher stress is necessary to start the transformation, it is also plausible that the negative slope of the second part on Fig. 7 should correspond to a negative slope on the  $d_i(T)$  functions. Indeed there is a slight decreasing tendency with increasing  $T$  on Fig. 9. Unfortunately, the accuracy of our present results does not allow a deeper and proper analysis of the field dependence of the dissipative terms. In addition, the details of the transformation (and thus the magnitude of  $d_i$ ) can be different for stress and temperature induced transformations as well as can also depend on the prehistory of the samples (not investigated here).

Finally Fig. 11 shows the  $d(\xi)$  function as calculated from the inverses of the normalized hysteretic  $\varepsilon$ – $T$  loops (see relations (8)) at different stress levels, while in Fig. 12 the twice of the integral of this for the whole thermal circle (i.e. between  $\xi = 0$  and  $\xi = 1$ ), 2D

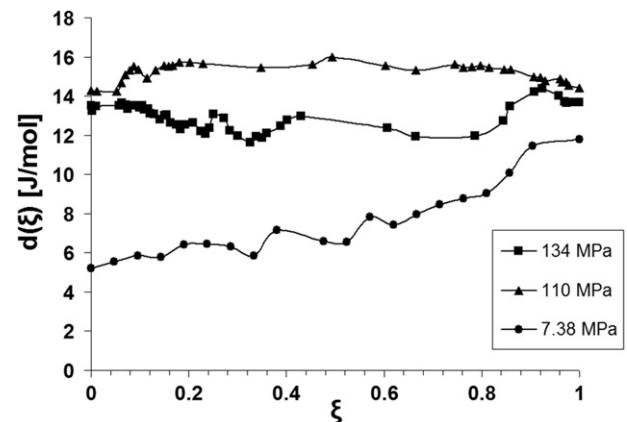


Fig. 11. Dissipative energy ( $d(\xi) = [d_0(\xi) + d_1(\xi)]/2$ ) term versus the transformed martensite fraction, calculated from the normalized  $\varepsilon$ – $T$  loops, at different stress levels.

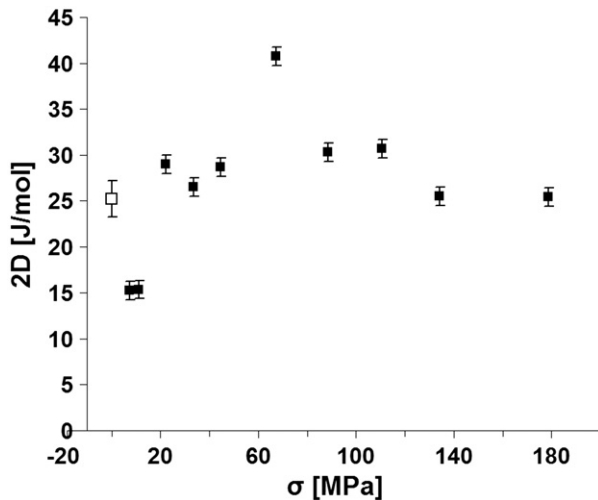


Fig. 12. Energy dissipated within one  $\varepsilon$ – $T$  hysteric loop as the function of  $\sigma$  (see also Fig. 8 in [17] with recalculated vertical axis, as mentioned at Fig. 6).

( $\sigma$ ) is plotted. The full dots in Fig. 12 show the values obtained from integration, while the open dot at  $\sigma = 0$  was calculated from the DSC curves (Fig. 1) according to the relation  $Q_{\downarrow} + Q_{\uparrow} = 2D$  ( $Q_{\downarrow} = -331.6$  J/mol,  $Q_{\uparrow} = 357.6$  J/mol). It can be seen that full dots fit self-consistently within the experimental errors to the open dot calculated from the independent (DSC) measurement. Furthermore the value of  $2D$  is constant within the experimental scatter and its average is about 24 J/mol.

## 5. Conclusions

The following conclusions can be drawn from our results.

- The transformation strain,  $\varepsilon^{\text{tr}}$ , determined from  $\varepsilon$ – $T$  loops, has an S-shape dependence on the stress.
- The transformation strain, determined from  $\sigma$ – $\varepsilon$  loops, depends on the temperature showing a similar saturation value (of about 6.1%) as obtained from  $\varepsilon$ – $T$  loops.
- i) and ii) reflects, according to eq. (6), a similar change in the relative fraction of stress induced martensite variants,  $\eta$ , versus  $\sigma$  and  $T$ , respectively.
- The dissipative energy terms (derivatives of the dissipative energy by the martensite volume fraction,  $\xi$ , at  $\xi = 0$  and  $\xi = 1$ ),  $d_0$  and  $d_1$ , were calculated from  $\varepsilon$ – $T$  loops and it was obtained that they are independent of  $\sigma$ , having an average value of 12 J/mol.
- The elastic energy terms (derivatives of the elastic energy by the martensite volume fraction,  $\xi$ , at  $\xi = 0$  and  $\xi = 1$ ),  $e_0$  and  $e_1$ ,

were calculated from  $\varepsilon$ – $T$  loops. They are  $\sigma$  dependent with slopes  $-0.25$  and  $-0.14$  J/mol MPa, respectively.

- Although the equilibrium transformation temperature,  $T_0$ , due to the stress dependence of  $\varepsilon^{\text{tr}}$ , is not a linear function at low stresses, the  $T_0(\sigma)$  function can be approximated by a straight line.
- The slope of  $T_0(\sigma)$  is different from the slopes of the start and finish temperatures and this difference is attributed to the stress dependence of  $e_0$  and  $e_1$ .
- The dissipative energy terms,  $d_0$  and  $d_1$ , were also calculated from  $\sigma$ – $\varepsilon$  loops and it was obtained that they are independent of  $T$ . Both have a value of about 4 J/mol and their value is lower for the  $\varepsilon$ – $\sigma$  loops by a factor of 3 than those obtained from the  $\varepsilon$ – $T$  loops.
- The elastic energy terms,  $e_0$  and  $e_1$ , were also calculated from  $\sigma$ – $\varepsilon$  loops and it was obtained that they have linear temperature dependence with slopes  $-0.55$  J/mol K and  $-0.18$  J/mol K, respectively.

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