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The Influence of Loading on the Heat of Transformation in Shape Memory Alloys

Standard caloric measurements on Shape Memory Alloys (SMAs) are usually carried out with the specimen in a state free of stress, by means of standard calorimeters. However, in its every application, the material is subjected to some load, being therefore necessary to investigate the influence of loading on the caloric behavior of SMAs, in order to take this into account when modeling their thermodynamic behavior. The present work investigates the influence of loading on the heat of transformation in SMAs. Experimental measurements were carried out on NiTi samples and a mathematical description of the observed behavior was developed. The theoretical results are in agreement with the experimental ones.

Keywords: Shape memory alloy, heat of transformation, martensitic phase transformation

Introduction

As far as the thermomechanical characterization of Shape Memory Alloys (SMAs) is concerned, it is usual to explore three sets of well known basic curves: the Load-Strain Curve under different constant temperatures (Figure 1a), the Strain-Temperature Curve under different constant loads (Figure 1b), and the Load-Temperature Curve under different constant strains, (Figure 1c).

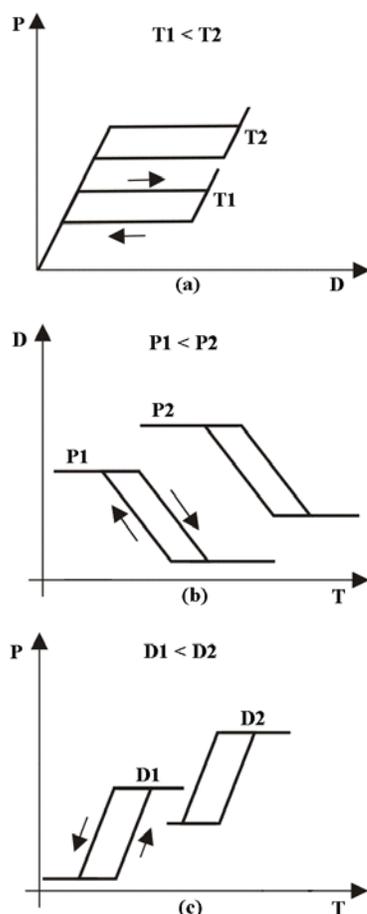


Figure 1. a) Load-Strain Curves. b) Strain-Temperature Curves. c) Load-Temperature Curves (Schematic).

Figure 1a shows two Load-Strain Curves at two different constant temperatures, denoted $T1$ and $T2$ and being $T1 < T2$. It is observed that the higher the temperature, the higher the loading necessary to induce the direct and reverse phase transformations. Two Strain-Temperature Curves under two different constant loads $P1$ and $P2$, being $P1 < P2$, are shown in Fig. 1b. The curves show that the higher the constant load, the higher the temperature necessary to induce the phase transformations. And, in Fig. 1c, there can be seen two Load-Temperature Curves under two different constant pre-strains $D1$ and $D2$, being $D1 < D2$. The curves show that the higher the constant pre-strain, the higher the load under which the phase transformation in both directions takes place (Da Silva, 2000; Glasauer, 1996). This last observation is very important to understand the experiments and results hereby presented.

It may be observed in the curves presented in Fig. 1 that the behavior of the SMA is always characterized by a hysteresis loop. This hysteretic behavior has been intensively investigated in the last decade (Xu, 1992; Glasauer, 1996). Xu (1992) investigated the size of the hysteresis, the temperature dependence on the hysteresis area, and the behavior inside the hysteresis loop within the elastic range in the Load-Strain diagram. He investigated Cu81.8Al14Ni (wt %) and Cu26Zn6.2Al (wt %) single crystals, and according to his work the size of the hysteresis does not depend much on the temperature, as long as the material undergoes a complete phase transformation in both directions (austenite to martensite and vice-versa). Glasauer (1996) investigated the quasi-plastic behavior under tension and compression, and the transition from quasi-plastic to pseudoelastic behavior of a Cu75Zn18Al sample (wt %). He observed that this alloy could present, at the same temperature, either a quasi-plastic or a pseudoelastic behavior, depending on the direction of the temperature change, that is, whether the intended test temperature was reached from a higher (after heating) or from a lower temperature level (after a cooling process). The reason for such a behavior has not been completely understood yet.

These two cited works only point out the major focus of a great number of works about the thermomechanical behavior of SMAs that have been carried out in the last years. On the other hand, the caloric behavior of these alloys has received much less attention, hence some important unanswered questions in this field. One of them concerns the influence of loading on the heat of transformation of these alloys, since when put to use they are usually made to work under certain loads and not free of stress as in the standard caloric measurements. In this context, the knowledge about the influence of loading on the heat of transformation may be of great importance for the development of SMA models based on thermodynamic theories.

Below the temperature M_f , the martensitic phase is the only stable one for SMAs. By heating an SMA sample up to a critical

temperature A_s , a phase transformation from martensite to austenite begins, finishing at A_f . During this transformation a certain amount of heat is absorbed by the sample (endothermic reaction). By cooling the material down to another critical temperature M_s , a reverse phase transformation from austenite to martensite begins. The martensitic transformation finishes when the critical temperature M_f is reached. During this transformation the heat absorbed by the sample during heating is now released (exothermic reaction) upon cooling. This heat absorbed during heating and released during cooling is called heat of transformation. The question here is to investigate the influence of loading on the caloric behavior of SMAs, which means to investigate the caloric behavior when the material undergoes a phase transformation under load. There are few reports concerning this matter and from none of them one can have a clear idea about the influence of loading on the heat of transformation in SMAs.

The aim of the present work is to investigate the influence of loading on the heat of transformation of a NiTi polycrystalline SMA by means of a standard calorimeter, and to mathematically describe the experimental results. In order to do so, a special specimen holder had to be developed. The calorimetric measurements were performed on a Ni50.2Ti (wt %) based SMA. The results were analyzed taking into account other thermomechanical experiments and the model for SMAs proposed by Achenbach-Müller (1982).

Nomenclature

- A = Austenite phase, dimensionless
- A_c = Coherency coefficient, J/kg
- A_s = Austenite start temperature, °C
- A_f = Austenite finish temperature, °C
- c = Specific heat, J/kg.K
- D = Strain, %
- d = Specific strain, D/m
- d_A = Specific strain of the austenitic phase, d_A/m
- d_m = Specific strain of the martensitic phase, d_m/m
- F = Free energy, J
- f = Specific free energy, J/kg
- f_A = Specific free energy of the austenitic phase, J/kg
- f_M = Specific free energy of the martensitic phase, J/kg
- m = Mass, kg
- M = Martensite phase, dimensionless
- M_+ = Martensite variant favored in tension, dimensionless
- M_- = Martensite variant favored in compression, dimensionless
- M_s = Martensite start temperature, °C
- M_f = Martensite finish temperature, °C
- P = Load, N
- s_A = Specific entropy of the austenitic phase, J/kg.K
- s_M = Specific entropy of the martensitic phase, J/kg.K
- T_R = Reference temperature, °C
- T = Temperature, °C
- u_A = Specific internal energy of the austenitic phase, J/kg
- u_M = Specific internal energy of the martensitic phase, J/kg
- z = Martensitic phase fraction, 1

Greek Symbols

- α = Specific elastic modulus, N/kg.m
- ΔF = Coherency energy, J
- Δf = Specific coherency energy, J/kg
- Δs = $s_A - s_M$, J/kg.K
- Δu = $u_A - u_M$, J/kg.K
- ε_A = Specific internal energy of austenite at $T = T_R$, J/kg
- ε_M = Specific internal energy of martensite at $T = T_R$, J/kg
- Σ = Entropy production, J/K.s
- σ = Specific entropy production, J/K.kg.s

- η_A = Specific entropy of austenite at $T = T_R$, J/kg.K
- η_M = Specific entropy of martensite at $T = T_R$, J/kg.K

Subscripts

- a relative to austenite
- m relative to martensite

Experimental Setup and Measurement Description

A Differential Scanning Calorimeter by Perkin Elmer (DSC7) was used to measure the heat of transformation. Due to the relative small dimensions of the calorimeter furnace (9.0 mm diameter and 7.0 mm depth) a special specimen holder had to be developed under these restrictions, in order to place the specimen under load. In practical terms, it means to put the specimen under a constant strain. This was possible using the developed specimen holder shown in Fig. 2, which consists of a two-piece block of Aluminum. The upper part (1) has four holes without thread and the bottom part (2) four holes with thread. The pre-strained specimen is placed between the two parts and these are fixed together by means of four bolts (3). The specimens were pre-strained by means of a tension machine developed in the Institute of Thermodynamics at the University of Berlin. This machine was especially developed to work with small dimension specimens (Glasauer, 1996). The analyzed material was a Ni50.2Ti (wt %) wire of 0.29 mm diameter.

The calibration of the calorimeter was performed following the standard procedure, but using two identical empty specimen holders instead of the standard capsules. After that, the calorimetric measurements were performed following the standard procedure. The specimens were heated and cooled within a temperature range from 10 to 120°C at 1°C/min.

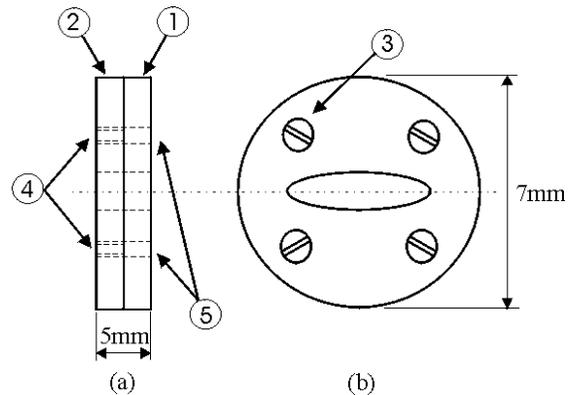


Figure 2. Developed Specimen holder.

Experimental Results and Discussion

In this section, some experimental results are presented and discussed. Figures 3 and 4 show the measured transformation temperatures A_s and M_s , respectively, under three different pre-strains. For each considered pre-strain a set of at least 30 measurements was carried out. The presented resulting values are average values for each set of measurements.

It may be observed that the temperatures of transformation increase with an increasing constant pre-strain.

In order to understand the results showed in Figures 3 and 4 one may analyze Load-Deformation Curves at different prescribed test temperatures, as shown in Fig. 5 for a Ni50Ti48Cu (wt %) sample at 25°C, 65°C and 100°C. It is clear that the higher the test temperature, the higher the load needed to induce the transformations. Another helpful experiment for understanding the increase in the transformation temperatures is the Strain-

Temperature Curve under different constant prescribed loads. Fig. 6 shows such curves for a Ni50.2Ti (wt %) sample under 4N and 12N. One may see that the higher the prescribed load, the higher the transformation temperatures. These two observations concerning Load-Deformation and Deformation-Temperature Curves are in accordance with the observed changes in the measured transformation temperatures obtained by means of the calorimetric measurements presented in Figures 3 and 4.

As one may observe from experimental Deformation-Temperature curves (under constant loads), the greater the prescribed strain, the higher the load under which the phase transformations take place (Figure 1c). From this observation one may conclude from Figures 3 and 4 that the greater the load, the higher the transformation temperatures.

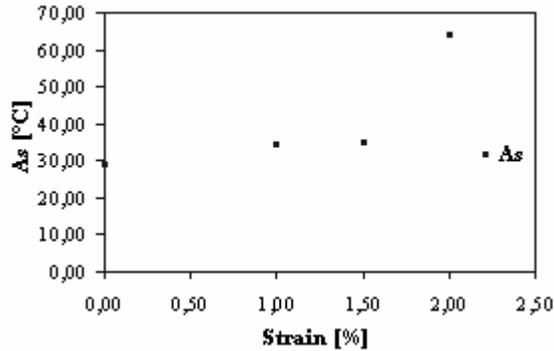


Figure 3. A_s for different pre-strains in Ni50.2Ti (wt %).

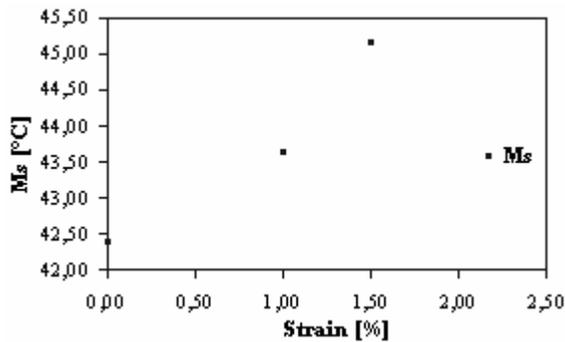


Figure 4. M_s for different pre-strains in Ni50.2Ti (wt %).

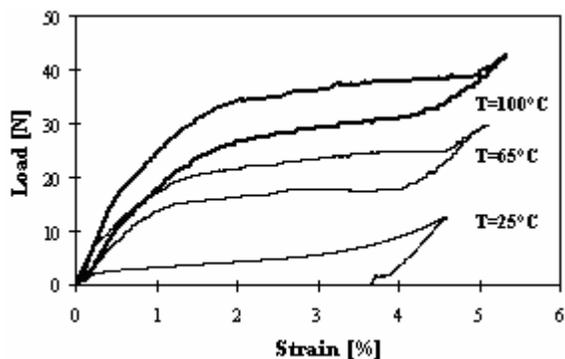


Figure 5. L-D Curves for Ni50Ti48Cu (wt %) for different temperatures (Da Silva, 2000).

Figure 7 shows the experimental results obtained for the heat of transformation under different pre-strains. It is observed that the heat of transformation shows an initial increase and a subsequent

decrease with an increasing pre-strain, or equivalently, with an increasing load.

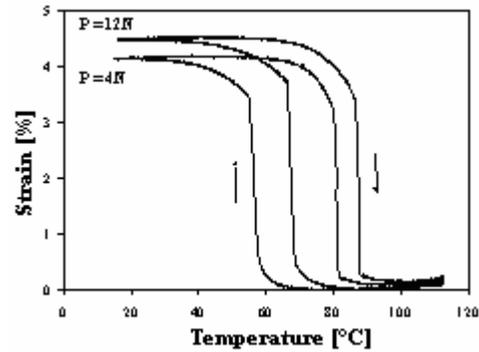


Figure 6. D-Temperature Curves for Ni51Ti (wt %) for different loads (Da Silva, 2000).

To understand this result, the model for SMAs proposed by Achenbach and Müller (1982) is considered here. The model takes into account three possible phases, being two of them variants of martensite and denoted by M_+ and M_- . The other one is the austenite one and denoted by A . The two variants of martensite are thermodynamically stable below M_s . This means that when the material is cooled below M_s in a state free of stress, the two variants of martensite nucleate and grow statistically at the same proportion. Under these conditions the specimen will have 50% of martensite M_+ and 50% of martensite M_- below M_f . This assumption is based on the self-accommodation nature of the martensitic phase transformation (Delaey, 1974). The austenite A is thermodynamically stable above A_s , which means that when the material is heated above A_s in a state free of stress, the austenite phase A will be the only stable one. Also, the martensite may be mechanically induced (Delaey, 1974). Below M_s the self-accommodated martensite variants may be reoriented and above A_s the austenite phase may be transformed into martensite by means of loading (Delaey, 1974). The model proposed by Achenbach and Müller (1982) assumes that under tensile loads the formation of the variant M_+ is favored. On the other hand, under compressive loads the formation of M_- is the favored one. When the specimen is subjected to a high enough tensile load below M_s the martensite variant M_- starts to reorient into M_+ . This transition continues as long as the load is high enough and until all M_- variants change into M_+ . After the unloading a quasi-plastic strain remains at 25°C, as shown in Fig. 5.

The result presented in Fig. 7 was analyzed based on these considerations. Firstly, the Load-Deformation curves at different constant prescribed temperatures shown in Figure 8 were considered, with a strain range from 1.0% to 3.6%. In a state free of stress and strain ($P = 0$ and $D = 0$) at $T = 25^\circ\text{C}$ the specimen is statistically composed of 50% of M_+ and 50% of M_- . The points A, B, C, D and E represent five quasi-plastic pre-strains corresponding to 0.5%, 1.0%, 2.0%, 3.0% and 3.6% respectively. The fractions of M_+ and M_- given in Figure 8 are assumed considering the Achenbach and Müller model (1982), as described above.

At $T = 100^\circ\text{C}$ in a state free of stress and strain ($P = 0$ and $D = 0$) only the austenitic phase is stable. Under a heavy enough loading the austenite transforms into stress induced martensite. The points A', B', C', D' and E' represent the states for the prescribed constant pre-strains (prescribed at $T = 25^\circ\text{C}$) after the heating from 25°C to 100°C. In these states the phases A and M_+ may coexist if the strain during the heating is held constant. Also, the fractions of austenite and martensite are also approximate values for

these states. The variant M_- transforms completely into austenite during the heating, independently of the prescribed deformation, so there is no variant M_- at points A', B', C', D' and E'. On the other hand, not all the M_+ variant transforms into austenite. Due to the load it is submitted to, part of it transforms directly into the stress-induced martensite M_+ at 100°C. Under this condition the martensite M_+ at 25°C contributes less or even not at all to the heat of transformation, once it is already in the martensitic state. Due to the fact that the fraction of martensite M_+ at 25°C increases with the increasing prescribed pre-strain, its contribution to the heat of transformation decreases with the increasing load. This explains why the heat of transformation decreases with the increasing pre-strain (load).

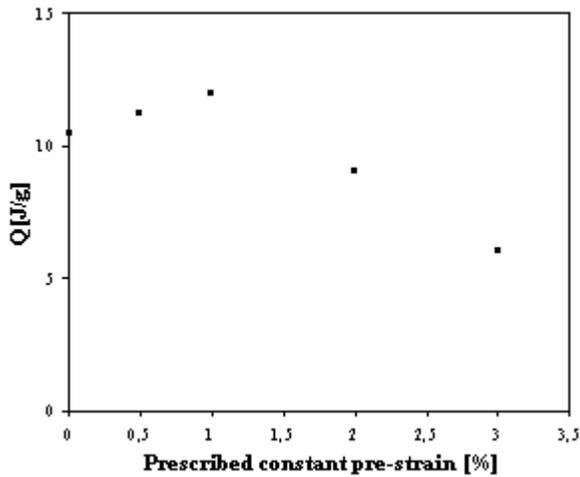


Figure 7. Heat of transformation under the prescribed strains (under load) for the Ni50.2Ti (wt %) sample – Upon heating.

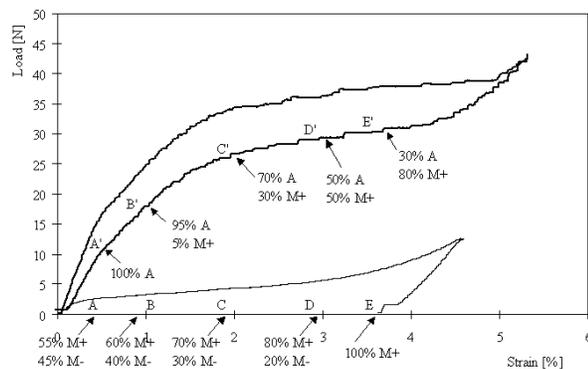


Figure 8. Graphic interpretation of the calorimetric results – Ni50%Ti48%Cu (wt %) (Da Silva, 2000).

If the prescribed strain at 25°C falls within the elastic range of the pseudoelastic curve at 100°C, approximately until 1.0%, then this analysis is not true. Within this range all martensite transforms into austenite upon heating. Therefore, the higher the pre-strain within this range, the greater the load under which the transformation takes place and the higher the heat needed to induce it. This explains the initial increase in the heat of transformation with an increasing load (Fig. 7).

Mathematical Description

The starting point of the mathematical description proposed here is the work presented by Huo et al (1993). Based on the 1st and 2nd

laws of thermodynamics and considering a quasi-static process the entropy production Σ can be written as

$$T\Sigma = P\dot{D} - S\dot{T} - \dot{F} \geq 0, \quad (1)$$

where P is the load, D the elongation, S the entropy, T the temperature and F the Helmholtz free energy. For a mixture of phases one may in general represent its free energy as the sum of the individual free energies. In this work F was considered as the sum of the free energies F_A and F_M of the austenite and martensite, respectively. Therefore, for a specimen composed of austenite and martensite one may write the specific energy as follows:

$$f = (1 - z)f(d_A) + zf(d_M) + \Delta f, \quad (2)$$

where $f(d_A) = F_A/m_A$, $f(d_M) = F_M/m_M$ and $z = m_M/m$. The masses of the phase A and M are m_A and m_M , respectively, m is the total mass and z is the martensite phase fraction. For $z = 1$ there is only martensite and for $z = 0$, only austenite. In the present description it is assumed that each interface contributes with the same amount to the coherency energy and that the number of interfaces is proportional to $z(1 - z)$. This is a simple expression that satisfies the necessary requirement that $\Delta f = 0$ holds for either $z = 0$ or $z = 1$. Thus, it is assumed that the specific coherency energy is given by

$$\Delta f = A_c z(1 - z), \quad (3)$$

where $A_c > 0$ is called the coherency coefficient, which is assumed positive so that there is a penalty for the formation of interfaces. Therefore, f is zero if either martensite or austenite is present.

Analogously to expression (2), it is assumed that the specific elongation is given by the expression

$$d = (1 - z)d_A + zd_M, \quad (4)$$

where d_A and d_M are the elongations of A and M respectively. The equations (1), (2) and (4) provide the following expression for the specific entropy production σ :

$$\begin{aligned} T\sigma = & \left(s + \frac{\partial f}{\partial T} \right) \dot{T} + (1 - z) \left(P - \frac{\partial f_A}{\partial d_A} \right) \dot{d}_A \\ & + z \left(P - \frac{\partial f_M}{\partial d_M} \right) \dot{d}_M \\ & + [P(d_M - d_A) - (f_M - f_A) - A_c(1 - 2z)] \dot{z} \geq 0, \end{aligned} \quad (5)$$

Material Equations

The specific values of the internal energies u_A and u_M and the specific entropies s_A and s_M of the phases A and M , respectively, may be written as

$$u_A(d_A, T) = \frac{1}{2} \alpha d_A^2 + c\Delta T + \varepsilon_A, \quad (6)$$

$$u_M(d_M, T) = \frac{1}{2} \alpha (d_M - \Delta_d)^2 + c\Delta T + \varepsilon_M, \quad (7)$$

$$s_A(T) = c \ln(T/T_R) + \eta_A, \quad (8)$$

$$s_M(T) = c \ln(T/T_R) + \eta_M, \quad (9)$$

where c and α are the common specific heat and elastic modulus of the phases A and M . T_R is a reference temperature and $\Delta T = (T - T_R)$. The ε 's and η 's are the values of u and s of the phases A and M

in the undeformed state at $T = T_R$. The energy and entropy differences between the martensitic and austenitic phases at $T = T_R$ are denoted by $\Delta\varepsilon = \varepsilon_M - \varepsilon_A$ and $\Delta\eta = \eta_M - \eta_A$ respectively. $\Delta\varepsilon$ and $\Delta\eta$ are negative because the phase change from M to A is endothermic. Thus, $\varepsilon_A > \varepsilon_M$ and $\eta_A > \eta_M$ hold too. For the mixture of phases, one has:

$$s = (1-z)s_A + zs_M. \quad (10)$$

From equations (6)-(10) one may write $F = u = Ts$ and

$$f_A = \frac{1}{2}\alpha d^2 + c\Delta T - R + \varepsilon_A - T\eta_A, \quad (11)$$

$$f_M = \frac{1}{2}\alpha(d - \Delta_d)^2 + c\Delta T - R + \varepsilon_M - T\eta_M, \quad (12)$$

where $R = cT \ln(T/T_R)$ and $\Delta_d = (d_M - d_A)$.

Partial Equilibrium

Reversible processes are those in which the entropy production (5) vanishes for all values of \dot{T} , \dot{d}_A , \dot{d}_M and \dot{z} (Huo et al., 1993). This means that the requirements for reversible processes are:

$$s = \partial f / \partial T, \quad (13)$$

$$P = \frac{\partial f_A}{\partial d_A} = \frac{\partial f_M}{\partial d_M} = \alpha d_A = \alpha(d - \Delta_d), \quad (14)$$

$$P\Delta_d - (f_M - f_A) = A_c(1-2z). \quad (15)$$

Equation (13) ensures the thermal equilibrium, which means that the temperature T is the same in every point of the specimen. Equation (14) ensures the dynamic equilibrium, which means that the load is equal in both phases A and M . And equation (15) ensures the phase equilibrium, that is, the material undergoes the phase transformation without hysteresis.

However, experiments show that the hysteresis is indeed present, which means that the phase equilibrium is not established during the transformations. Therefore, when inserting (11) and (12) into (5), one obtains an expression for the entropy production in the form of

$$T\sigma = [P\Delta_d - (\Delta\varepsilon - T\Delta\eta) - A_c(1-2z)]\dot{z} \geq 0, \quad (16)$$

which is the expression for the entropy production without phase equilibrium.

Description of the P-T-Diagram

In the Load-Deformation Diagram (P-T-Diagram) the specimen is firstly deformed in the martensitic state. The generated quasi-plastic deformation d_V is fixed and the body heated through the transformation temperatures T_{RB} (Austenite start temperature) and T_{RE} (Austenite finish temperature), and cooled through T_{FB} (Martensite start temperature) and T_{FE} (Martensite finish temperature). Figure 9 shows a schematic P-T-Diagram, whereby the dashed lines represent the phase transformation without phase equilibrium, and the thick lines show the phase transformation with phase equilibrium. Upon heating, the material tries to recover its original configuration, being then constrained by the specimen holder and thus exerting a force against it.

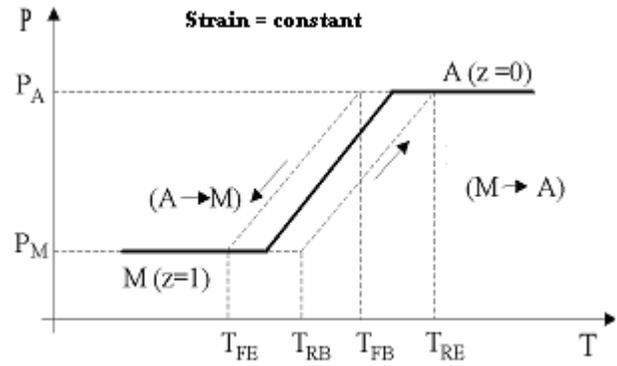


Figure 9. Schematic P-T-Curve.

Transformation Temperatures

Considering the situation depicted in Fig. 9, the load in fully martensitic and austenitic phase are denoted by P_M and P_A respectively. According to Equation (14) the following equations hold:

$$P_M = \alpha(d - \Delta_d) \quad (\text{For the } M \text{ phase}), \quad (17)$$

$$P_A = \alpha d \quad (\text{For the } A \text{ phase}). \quad (18)$$

It is assumed that the phase equilibrium dominates the process at the beginning of the direct and reverse transformations. Hence, one may obtain P_M and P_A from the equation (15) with $z = 1$ and $z = 0$, respectively:

$$P_M = \frac{1}{\Delta_d}(\Delta\varepsilon - T_{RB}\Delta\eta - A_c), \quad (19)$$

$$P_A = \frac{1}{\Delta_d}(\Delta\varepsilon - T_{FB}\Delta\eta + A_c). \quad (20)$$

Eliminating P_M from (17) and (19), and P_A from (18) and (20), one obtains T_{RB} and T_{FB} , respectively, as functions of the pre-strain d_V as follows:

$$T_{RB} = \frac{1}{|\Delta\varepsilon|}[\alpha(d_V - \Delta_d)\Delta_d - \Delta\varepsilon + A_c], \quad (21)$$

$$T_{FB} = \frac{1}{|\Delta\varepsilon|}(\alpha d_V \Delta_d - \Delta\varepsilon - A_c). \quad (22)$$

To calculate T_{FE} and T_{RE} it is still necessary to obtain the slope dP/dT of the dashed ascending and descending lines in Fig. 9. It is assumed that both of them are parallel to the phase equilibrium one (thick line), which is obtained without the coherency energy. Making $A_c = 0$ in (15) results in:

$$P(T) = \frac{1}{\Delta_d}(\Delta\varepsilon - T\Delta\eta). \quad (23)$$

It follows for the direct and reverse transformations, respectively, that

$$P_F(T) = \frac{1}{\Delta_d}(\Delta\varepsilon - T\Delta\eta + A_c), \quad (24)$$

and

$$P_R(T) = \frac{1}{\Delta_d}(\Delta\varepsilon - T\Delta\eta - A_c). \quad (25)$$

With $P_F = P_M$ in (24) and $P_R = P_A$ in (25), it follows with (19) and (20), respectively, that

$$T_{RE} = \frac{1}{|\Delta\eta|}(\alpha d_V \Delta d - \Delta\varepsilon + A_c), \quad (26)$$

$$T_{FE} = \frac{1}{|\Delta\eta|}[\alpha(d_V - \Delta d)\Delta d - \Delta\varepsilon - A_c]. \quad (27)$$

One may see that T_{RB} , T_{RE} , T_{FB} and T_{FE} increase with d_V . This agrees with the experimental results presented in Figures 3 and 4, whereby it is shown that the higher the pre-strain, the higher the phase transformation temperatures.

Heat of Transformation

Under the assumption that in the direct and reverse transformations the phase fraction z changes linearly with the load P , and taking into account (17) and (18), one has

$$P = \alpha(d_V - z\Delta d) \Rightarrow z = \frac{d_V}{\Delta d} - \frac{P}{\alpha\Delta d}. \quad (28)$$

Inserting (24) and (25) in (28), the right side of (28) becomes an explicit linear function of T , and one may obtain the following relations:

$$T_F(z) = \frac{1}{|\Delta\eta|}(\Delta\varepsilon + A_c - \alpha d_V \Delta d) + \frac{1}{|\Delta\eta|} \Delta d^2 z, \quad (29)$$

$$T_R(z) = \frac{1}{|\Delta\eta|}(\Delta\varepsilon - A_c - \alpha d_V \Delta d) + \frac{1}{|\Delta\eta|} \Delta d^2 z. \quad (30)$$

According to the second law of thermodynamics the specific heat flux is given by

$$\dot{q} = T \frac{ds}{dt} - T\sigma. \quad (31)$$

Equations (8) through (10) and (16) give

$$\dot{q} = c\dot{T} - [P\Delta d - \Delta\varepsilon - A_c + 2Az]\dot{z}. \quad (32)$$

The right side of (32) becomes a function of z and \dot{z} through the insertion of P in (28) and $\dot{T} = (\alpha\Delta d^2/|\Delta\eta|)\dot{z}$ in (29) or (30). Hence:

$$\dot{q} = \left\{ c \frac{\alpha\Delta d^2}{|\Delta\eta|} - [\alpha d_V \Delta d - \Delta\varepsilon - A_c] \right\} \dot{z} + \left[\frac{1}{2} \alpha \Delta d^2 - A_c \right] (\dot{z})^2. \quad (33)$$

To calculate \dot{q} during the heating (reverse transformation) the range from $z = 1$ to $z = z_E$ is considered and during the cooling (direct transformation) from $z = z_E$ to $z = 1$. The martensite fraction that forms upon heating is z_E and it depends on the final temperature and on the pre-strain d_V . Finally, one obtains:

$$Q_F = \left(\frac{c\alpha\Delta d^2}{|\Delta\eta|} + \Delta\varepsilon + A_c - \alpha d_V \Delta d \right) K + B, \quad (34)$$

$$Q_R = - \left(\frac{c\alpha\Delta d^2}{|\Delta\eta|} + \Delta\varepsilon + A_c - \alpha d_V \Delta d \right) K - B, \quad (35)$$

where $K = (1 - z_E)$ and $B = (1/2\alpha\Delta d^2)$. The main term $\Delta\varepsilon < 0$ is much greater than the other terms in (34). It is therefore clear that Q_F is negative, as expected, because the transformation $A \rightarrow M$ is exothermic. It is thus clear that $Q_F = -Q_R$ holds too.

Dependence of the Transformation Heat on d_V

The term $(1 - z_E)$ in (34) and (35) depends on d_V as well as on the final temperature. It is then necessary to estimate the size of the phase fraction z_E , which remains after the heating. For the NiTiCu alloy one may do so from Fig. 10: $d_V = 0.5\%$: $z_E = 0.0$, $d_V = 2.0\%$: $z_E = 0.3$ and $d_V = 3.6\%$: $z_E = 0.8$. To express these experimental values in an analytical form one may consider the idealized pseudoelastic hysteresis loop depicted by the straight lines in Fig. 10.

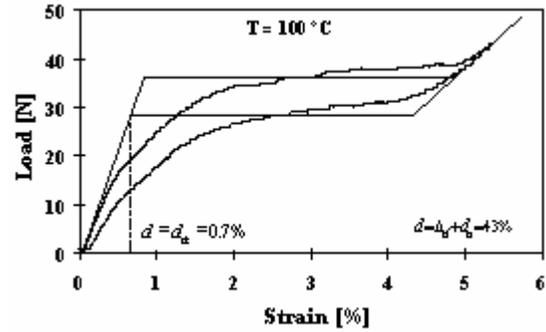


Figure 10. P-D-Diagram for NiTiCu at 100°C.

One then has:

$$z_E = \frac{d_V - d_a}{\Delta d} \quad (\text{for } d_V \geq d_a), \quad (36)$$

$$z_E = 0 \quad (\text{for } d_V < d_a). \quad (37)$$

For $d_V < d_a$ equation (35) gives

$$Q_R(d) = \frac{c\alpha\Delta d^2}{|\Delta\eta|} + |\Delta\varepsilon| - \frac{1}{2}\alpha\Delta d^2 + \alpha d_V \Delta d. \quad (38)$$

For $d_V > d_a$ one obtains:

$$Q_R(d_V) = Q_R(d_a) - \left(|\Delta\varepsilon| + \frac{c\alpha\Delta d^2}{|\Delta\eta|} \right) \frac{d_V - d_a}{\Delta d} + \alpha(\Delta d - d_a)(d_V - d_a) - \frac{1}{2}\alpha(d_V - d_a)^2 + A \frac{d_V - d_a}{\Delta d} \left(1 - \frac{d_V - d_a}{\Delta d} \right). \quad (39)$$

Analyzing (38) and (39), one concludes that Q_R increases with d_V while $d_V \leq d_a$, since only the term containing d_V in (38) is not constant. When $d_V > d_a$ the term Q_R will decrease with d_V , because in (39) the decreasing linear term with $\Delta\varepsilon$ is the main one. This result agrees with the experimental one presented in Fig. 7.

Concluding Remarks

The heat of transformation under loading on a Ni50.2Ti (wt %) Shape Memory Alloy was measured by means of a special specimen holder, which allowed the fixation of a constant pre-strain by standard calorimetric measurements. The pre-strains were

previously prescribed to the specimens with the use of a tension machine. The results showed that the temperatures of transformation increase with an increasing pre-strain. The heat of transformation also increases with the loading as long as the elastic range of the austenitic phase (upon heating) is not exceeded. Outside this range, a decrease of the heat of transformation with an increasing pre-strain (or load) was observed. By analyzing other curves such as the Load-Deformation for different temperatures and the Deformation-Temperature for different loads, and making some assumptions about the Achenbach-Müller model, one is able to understand the reasons for this behavior and to mathematically describe the observations. The theoretical results agreed with the experimental ones.

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References

Achenbach M., Müller I., 1982, "A model for Shape Memory", *Journal de Physique*, C4, Tome 43, pp. 163-167.

Da Silva, E.P. Zur Kalorimetrie von Gedächtnislegierungen und zu ihrer Anwendung als elektrisch aktivierten Aktuatoren. PhD. Thesis, Technische Universität Berlin, Germany, 108 p.

Delaey L., Krishnan R.V., Tas H., 1974, "Thermoelasticity, pseudoelasticity and memory effects associated with martensitic transformations – Part I – Structural and microstructural changes associated with the transformations", *Journal of Materials Science* Vol. 9, pp. 1521-1535.

Glasauer, F.U., 1996, "Gächtnislegierungen – Experimentelle Untersuchungen und Aufbau einer Wärmekraft-maschine", PhD. Thesis, Technische Universität Berlin, Germany, 331 p.

Huo Y., Muller I., Seelecke S., 1993, "Quasiplasticity and pseudoelasticity in Shape Memory Alloys", *Lecture Notes in Mathematics*, Ed. Springer Verlag, Berlin, Germany, 291 p.

Xu X., 1992, "Experimentelle und theoretische Untersuchung des Hystereseverhalten in Formgedächtnis-legierungen", PhD. Thesis, Technische Universität Berlin, Germany, 212 p.

Planes, A., Macqueron, J.L., Morin, M., Guénin, G., 1981, "Study of martensitic transformation of a Cu-Zn-Al alloy by coupled enthalpy and acoustic emission measurements", *Phys. Status Solidi*, Vol. 66, pp. 717-724.

Sade M., Cesari, E., Hornbogen, E., 1989, "Calorimetry of a Cu-Zn-Al single crystal during pseudoelastic transformation", *J. Mat. Sci. Letters*, Vol. 8, pp. 191-193.

Wollants, P., De Bonte, M., Ross, R.J., 1983, "The stress-dependency of the latent heat of transformation in a beta-CuZnAl single crystal", *Z. der Metallkunde*, B and 74, Heft3 (2), pp. 127-131.