THERMOMECHANICS OF TRANSFORMATION
PSEUDOELASTICITY AND SHAPE
MEMORY EFFECT IN ALLOYS

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Abstract — Transformation pseudoelasticity and shape memory effect of alloy materials are investigated from the thermomechanical point of view. The thermomechanical constitutive equations and the kinetics of transformation established by the theory are applied to explain the stress-strain-temperature behavior of the material. Numerical illustrations for the uniaxial stress state are given.

I. INTRODUCTION

When a certain metallic material is stressed at a temperature level, the inelastic deformation observed on loading is completely recovered in the unloading process. At another temperature level the same material behaves quite differently. The stress-strain curve is now quite similar to that of the plastic material, and some amount of strain remains after a successive loading and unloading process. The residual strain is, however, recovered in the subsequent heating process. The former phenomenon is called the transformation pseudoelasticity, and the latter, the shape memory effect, which are both due to the shear deformation associated with the thermoelastic martensitic transformation and its reverse transformation of the material (DELAEY, KRISHNAN, TAS & WARLIMONT [1974]; PERKINS [1975]; SCHETKY [1979]).

The phenomena have been investigated metallurgically in great detail since the shape memory effect was first observed in Ti-Ni alloy in 1962. Cu-based alloys, In-based alloys and austenite steels also attract notice of the metallurgists. The application of the phenomena is widely recognized not only in the engineering field but also in the medical field (SCHETKY [1979]).

Some attempts have been made from the point of view of thermomechanics to describe the transformation pseudoelasticity and the shape memory effect of alloys. FALK [1980, 1983] first pointed out the analogy between the stress-strain curves of the materials which exhibit these phenomena and the electric field-polarization curves in the ferroelectric materials or the magnetic field-magnetization curves in the ferromagnetic materials, and demonstrated that Landau’s theory of phase transition (LANDAU & LIFSHITZ [1969]) could be well applied to the pseudoelasticity and the shape memory effect. On the other hand MULLER & WILMANSKI [1980, 1982] presented a quite different theory which is deeply based on statistical mechanics to explain the deformation of shape memory alloys at various temperature levels. The creep and yield of the material which is in the course of the martensitic transformations were recently investigated by means of a theory (ACHENBACH & MULLER [1983]).
In this study we try to construct a thermomechanical framework which covers the transformation pseudoelasticity and the shape memory effect associated with the stress-induced martensitic transformation and its reverse transformation (Nishiyama [1978]; Tamura [1982]). Following Tanaka & Nagaki [1982] the extent of transformation is regarded to be characterized by an internal state variable. The thermomechanical constitutive equations and the kinetics of transformation are derived as a consequence of Clausius-Duhem inequality. The transformation strip in the stress-temperature plane is introduced to give a pictorial view of the transformation phenomenology. The stress-strain-temperature curves of the material and the shape recovery on heating are examined both theoretically and numerically.

At present our attention is limited to the macroscopic behavior of the polycrystalline alloys. The crystallographic structural change during the transformations (Delaey et al. [1974]) is, therefore considered only indirectly. It should also be noted that the martensite-martensite transformation (Delaey et al. [1974]; Otsuka & Shimizu [1981]) is not taken into account, though it is important to estimate the deformation behavior of materials under the transformation starting point, $M_s$, in which temperature range some amount of the thermal-induced martensite exists before loading. Construction of a general theory which is based on both the stress-induced martensitic transformation and the martensite-martensite transformation will be the subject of a separate report.

II. BASIC EQUATIONS

Let us consider an alloy material which is in the course of thermoelastic martensitic transformation or of its reverse transformation.

The motion of a material point $X$ in the alloy is written as

$$x = x(X, t) .$$

The energy balance and the Clausius-Duhem inequality in the current configuration are expressed as

$$\rho \dot{U} - T : L^T + \text{div} \mathbf{q} - \rho \sigma = 0 ,$$

$$\rho \dot{\eta} - \rho \frac{\sigma_i}{\theta_i} + \text{div} \left( \frac{\mathbf{q}}{\theta} \right) \geq 0 .$$

The symbols in eqns (1) and (2) have the following physical significance:

- $x, X =$ position vectors of a material point $X$ in the current and the reference configurations, respectively,
- $t =$ time,
- $F = \partial x/\partial X =$ deformation gradient ($\det F > 0$),
- $L = F \cdot F^{-1} =$ velocity gradient,
- $E = (F^T \cdot F - I)/2 =$ Green strain tensor,
- $U =$ internal energy density,
- $T =$ Cauchy stress tensor,
- $\rho, \rho_o =$ densities in the current and the reference configurations, respectively,
- $\mathbf{q} =$ heat flux vector,
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\[ \sigma = \text{heat production term}, \]
\[ \theta = \text{temperature}, \]
\[ \eta = \text{entropy density}. \]

Throughout this study the notations \( \text{div} \) and \( \text{Div} \) stand for the divergence with respect to \( x \) and \( X \), respectively, and \( \text{Grad} \) means the gradient with respect to \( X \). The superposed dot means the material time derivative.

III. CONSTITUTIVE EQUATIONS

We assume that the Cauchy stress tensor \( \mathbf{T} \) and the entropy density \( \eta \) can be fully described by a set of variables

\[ j = (E, \theta, \xi) . \]

The variable \( \xi \) represents the extent of transformation, which corresponds to the internal state variable in continuum mechanics (Coleman & Gurtin [1967]; Tanaka & Nagaki [1982]). Since only two phases, austenite and martensite, appear in the present study, \( \xi \) can be regarded as the fraction of the produced phase. The original phase occupies, therefore, the rest, \( 1 - \xi \). The transformation rate \( \dot{\xi} \) and the heat flux \( q \) are proposed to be determined by the dissipation inequality.

By employing Helmholtz free energy

\[ \Psi(j) = U - \eta \theta , \]

and making use of eqn (2)_1, we can rewrite Clausius-Duhem inequality (2)_2 in the reference configuration. The result reads

\[ (K - \rho_0 \Psi_E) \dot{\mathbf{E}} - \rho_0 (\eta + \Psi_\theta) \dot{\theta} - \rho_0 \Psi_\xi \dot{\xi} - \frac{1}{\theta} \mathbf{Q} \cdot \text{Grad} \theta \geq 0 , \]

where we have introduced the following material quantities:

\[ K \equiv (\rho_0/\rho) \mathbf{F}^{-1} \cdot \mathbf{T} \cdot (\mathbf{F}^{-1})^T , \]
\[ \mathbf{Q} \equiv (\rho_0/\rho) \mathbf{q} \cdot (\mathbf{F}^{-1})^T . \]

Unless otherwise stated the suffix represents the partial differentiation, i.e., \( \Psi_E = \partial \Psi/\partial E \), etc.

In order that Ineq. (4) holds for all processes the formulae

\[ K = \rho_0 \Psi_E , \quad \eta = -\Psi_\theta , \]
\[ A \dot{\xi} - \frac{1}{\rho_0} \mathbf{Q} \cdot \text{Grad} \theta \geq 0 , \]

must be imposed, where the quantity \( A = -\Psi_\xi \) is called the affinity or the driving force of the transformation (Nishiyama [1978]).
According to the thermodynamics of continua by EDELEN [1974] and ERingen [1975], the dissipation inequality (5) assures us the existence of a scalar function 

$$\Phi = \Phi(A, \text{Grad} \theta; j)$$

which is called the dissipation potential, and the formulae

$$\dot{\xi} = \Phi_A, \quad -\frac{1}{\rho_\theta} Q = \Phi_{\text{Grad} \theta},$$

are obtained in terms of $\Phi$. Equation (6), represents the evolutional equation for the extent of transformation, that is, the kinetics of transformation, while eqn (6), governs the heat flow.

In order to progress further we study here the case in which the dissipation potential has such a structure as

$$\Phi = \tilde{E}(j)A^2/2 + 2\psi(\text{Grad} \theta; j).$$

In the above equation $\tilde{E}$ is a positive material function, while the subpotential $2\psi$ has the property such that $2\psi > 0$, and the equality holds only when $\text{Grad} \theta = \mathbf{0}$. Equations (6) and (7) combine to yield the governing equations

$$\dot{\xi} = \tilde{E}(j)A(j) = \tilde{E}(K, \theta; \xi),$$

$$-Q/(\rho_\theta \theta) = 2\psi_{\text{Grad} \theta}$$

The last equality in eqn (8), can be understood when the one-to-one correspondence of the reversible process, eqns (5), is taken into account.

Experimental observation reveals that the martensitic transformation and its reverse transformation are diffusionless in nature (NISHIYAMA [1978]). In other words the transformation kinetics (8), should be solved to be

$$\xi = \tilde{E}(K, \theta)$$

The argument $K$ in eqn (9) enables us to describe the transformation induced by the stress (NISHIYAMA [1978]; TAMURA [1982]). It should be noted that the kinetics (9) has the different forms in the martensitic transformation and the reverse transformation. The transformation pseudoelasticity discussed later depends on the irreversibility stems from this.

The point $(K, \theta)$ in the stress-temperature space which satisfies

$$0 = \tilde{E}(K, \theta)$$

represents the starting point of the transformation. On the other hand the point at which the transformation is completed is obtained by

$$1 = \tilde{E}(K, \theta).$$
We note that the condition
\[ \dot{\xi} \geq 0 \] (12)
holds during the process.

From eqns (5), (9) we can obtain the constitutive equation in rate-type. The results are as follows:
\[ \dot{K} = D: \dot{E} + \Theta + \Omega \dot{\xi} , \]
\[ \rho_o \dot{\eta} = -\Theta: \dot{E} + c \dot{\theta} + \Gamma \dot{\xi} , \] (13)
\[ \dot{\xi} = \varepsilon_K: \dot{K} + \varepsilon_\theta \dot{\theta} , \]
where the coefficients
\[ D = \rho_o \Psi_{EE} , \quad \Theta = \rho_o \Psi_{E\theta} , \quad \Omega = \rho_o \Psi_{E\xi} , \quad c = -\rho_o \Psi_{\theta\theta} , \quad \Gamma = -\rho_o \Psi_{\theta\xi} \]
are in general functions of \( \gamma \).

IV THERMOMECHANICS IN THE COURSE OF TRANSFORMATION (UNIAXIAL BEHAVIOR)

In this section the general theory developed in the preceding section is applied to the explanation of the uniaxial thermomechanical behavior of the alloys which are in the process of stress-induced martensitic transformation or of its reverse transformation.

Hereafter for simplicity the fraction of martensite is always denoted by \( \xi \) and then the fraction of austenite by \( 1 - \xi \) both in the course of martensite and reverse transformations.

**Stress and strain increments**

At the uniaxial tensile tests under a constant temperature, eqn (13) reduces to
\[ \dot{K} = D \dot{E} + \Omega \dot{\xi} . \] (14)

When it is integrated along the path in the course of martensitic transformation, we obtain
\[ \Delta K = \int_0^{t^*} D \dot{E} dt + \Omega , \] (15)
where \( t^* \) stands for the time when the transformation completes, while \( \Delta K \) represents the stress increment during the transformation, i.e., \( \Delta K = K(t^*) - K(0) \). It should be noted here that since the volume expansion is associated with the martensitic transformation, the material constant \( \Omega \) is negative, \( \Omega < 0 \).

The material constant \( D \) may be expressed as
\[ D = \lambda D + (\mu D - \lambda D)\xi, \]

when \( \lambda D \) and \( \mu D \) are referred to as the elastic constants of the austenite and the martensite, respectively. If \( \lambda D = \mu D = \text{constant} (= \bar{D}, \text{say}) \) is assumed, eqn (15) yields

\[ \Delta K = \bar{D} \Delta E + \Omega, \quad (16) \]

where \( \Delta E = E(t^*) - E(0) \) means the strain increment during the transformation.

Figure 1(a) illustrates the situation expressed in eqn (16). From \( o \) to \( a \) at which the martensitic transformation starts the figure shows that the elastic deformation of the austenite is governed by

\[ \dot{K} = \bar{D} \dot{E}. \quad (17) \]

The transformation progresses along the part \( ab \), and completes at \( b \). From \( b \) the elastic deformation again follows through eqn (17), but of the martensite this time.

In the course of reverse transformation associated with the unloading process, \( \xi \) changes from 1 to 0. Then from eqn (14), we obtain the following relation:

\[ \Delta K = \int_0^{t'} \bar{D} \dot{E} dt - \Omega \]

The counterpart of eqn (16) is:

\[ \Delta K = \bar{D} \Delta E - \Omega, \quad (18) \]

where \( \Delta K < 0 \) and \( \Delta E < 0 \) should be noted. The stress-strain behavior in the process is sketched in Fig. 1(b).

For the reverse transformation induced by the temperature increase above the point \( A_f \) under the stress-free state, we can obtain from eqn (13),

\[ 0 = \int_0^{t'} \bar{D} \dot{E} dt + \int_0^{t'} \bar{\Theta} \dot{\theta} dt - \Omega, \]

Fig 1 Stress-strain curve in the course of martensitic or reverse transformation
which reduces to

\[ 0 = \bar{D} \Delta E + \bar{\Theta} \Delta \theta - \Omega, \tag{19} \]

when the material constant \( \Theta \) is assumed to be constant (\( \bar{\Theta} \), say) throughout the process. Equation (19) determines the strain increments due to the temperature increment \( \Delta \theta \). In general, like \( D \), we can put

\[ \Theta = \lambda \Theta + (\lambda \Theta - \lambda \Theta) \xi \]

by making use of the material constants \( \lambda \Theta \) and \( \lambda \Theta \) of the austenite and the martensite, respectively.

When the deformation is constrained in the course of the reverse transformation, the thermomechanical behavior of material is governed by

\[ \int_0^\tau \dot{K} \, dt = \bar{\Theta} \Delta \theta + \Omega (\xi - 1). \tag{20} \]

This formula will be used later.

**Transformation phenomenology**

We examine here the transformation kinetics expressed by Koistinen & Marburger [1959], and Wang & Inoue [1983]

\[ \xi = 1 - \exp\left[ M_a (M_s - \theta) + M_b K \right] \tag{21} \]

in the uniaxial tensile stress state \( K \) with the condition

\[ M_a (M_s - \theta) + M_b K \leq 0, \]

which reduces to

\[ K \geq \left( \frac{M_a}{M_b} \right) (\theta - M_s). \tag{22} \]

The equality means the transformation starting line [cf. eqn (10)]. The condition (12), only under which the transformation undergoes, reads now as

\[ M_b K - M_a \theta \leq 0 \tag{23} \]

Transformation completing line is obtained by means of eqn (11) to be

\[ K = -2 \ln 10 / M_b + \left( \frac{M_a}{M_b} \right) (\theta - M_s), \tag{24} \]

where we employed a criterion, which is commonly used in metallurgy, that the completion of transformation is defined when \( \xi \) reaches 0.99. Equations (22) and (24) show that the transformation starting and completing lines are parallel in the \( K-\theta \) plane. Their slope \( M_a / M_b \) may depend on the temperature. Some experimental observations re-
vealed that the transformation starting was a straight line in the $K-\theta$ plane (Pops [1970]; 
Krishnan & Brown [1973]).

The region between the lines may be referred to as the transformation strip. The width
of the strip along the stress axis, $\Delta K_M$, is calculated to give

$$\Delta K_M = -2\ln 10/\overline{M} \overline{b} ,$$

which implies $\overline{M} \overline{b} < 0$.

The intersection of the transformation completing line (24) with the stress-free state
(the abscissa) is no other than the point $M_f$. Hence the following relation is obtained.

$$M_f a = -2\ln 10/(M_s - M_f) ,$$

which means $M_f a$ is also negative; $M_f a < 0$.

The same discussion for the reverse transformation gives us the following results:

Transformation kinetics:

$$1 - \xi = 1 - \exp[4a(A_s - \theta) + 4\overline{b}K]$$

Condition imposed on eqn (27):

$$K \leq -(4a/4\overline{b})(\theta - A_s) , \quad 4\overline{b}K - 4a\theta \geq 0 .$$

Transformation completing line:

$$K = -2\ln 10/4\overline{b} + (4a/4\overline{b})(\theta - A_s) .$$

Width of transformation strip:

$$\Delta K_A = 2\ln 10/4\overline{b} .$$

Formula for the $A_f$ point:

$$4a = 2\ln 10/(A_f - A_s) .$$

Equations (30) and (31) reveal that $4a > 0$ and $4\overline{b} > 0$.

An example of the transformation strips introduced above is sketched schematically
in Fig. 2 (Krishnan & Brown [1973]; Delaey et al. [1974]).

Pseudoelasticity and shape memory effect

Figure 3 illustrates the stress-strain curves at different temperature levels when the
transformation behavior is assumed as shown in Fig. 2, and $\overline{A}D = \overline{M}D = \overline{D}$. At $\theta = \theta_3$
the material exhibits the full pseudoelasticity. At $\theta = \theta_2$, however, the reverse transforma-
tion does not complete even when the stress-free state is attained in the unloading
process. The behavior is sometimes called the partial pseudoelasticity (Delaey et al.
[1974]) because it is a transition state from the full pseudoelasticity to the shape mem-
ory effect explained below. At $\theta = \theta_1$ no reverse transformation starts during the pro-
cess, and a certain amount of strain remains, which stems from the crystallographic structural change due to the martensitic transformation. The stress-strain relation below the point $M_s$ is not discussed here because the reorientation of the martensite plates; martensite-martensite transformation, which becomes essential in this temperature range is not taken into account (cf. Sec. I).

Figure 3(c) also shows a locus of the generic point in the $\theta$-$E$ plane when, after the loading and unloading isothermally at $\theta_1$, the specimen is heated to above the point $A_f$ under the stress-free state. The sections $ab$ and $ac$ in the curve represent the thermal expansion, while $bc$ stands for the contraction associated with the reverse transformation. Since the relation $|\partial / \partial \theta | \gg |(\partial / \partial \theta) \cdot \Delta \theta |$ always holds, the thermal expansion can be neglected compared to the transformation contraction. This means that the residual strain is fully recovered at the point $A_f$ (cf. eqn (20)).

We next consider the thermomechanical behavior of the material in the following process (Eisenwasser & Brown [1972]; Delaey et al. [1974]): Further deformation is restricted at the point $\theta$ in Fig. 3(c) while the temperature increases from $\theta_1$ to $\theta$ above the point $A_f$. The restriction is then released at $\theta = \theta$. From $\theta_1$ to $A_f$ nothing happens except for the thermal expansion of the martensite, which produces a compression stress $|\partial (A_s - \theta_1)|$ since the deformation is constrained. The amount is however small enough to be neglected when compared with the term which stems from the reverse transformation. Above the point $A_f$, the reverse transformation undergoes and the transformation contraction occurs, which results in the increase in tension stress. A path of the generic point in the transformation strip would be the thick solid line in Fig. 4. The path is determined by eqns (13) or (22) and (29), which can be rewritten as

$$K = \tilde{\theta}(\theta - A_s) + \Omega(\xi - 1) ,$$

$$K = (\frac{a}{A_s} \tilde{\theta})(\theta - A_s) + \ln \frac{\xi}{A_s} .$$

Both equations represent a straight line in the $K$-$\theta$ plane (cf. Fig. 4). The intersection of the lines gives a generic point $(K, \theta)$ corresponding to a fraction $\xi$. The point on the transformation completing line is obtained for $\xi = 0.01$ to be.
The stress $\bar{R}$ (the recoverable force, say) plays a very important factor to be considered when the actuators are designed with the shape memory alloys. It should be noted that practically all the martensite has transformed to the austenite at $\bar{R}, \bar{\theta}$. Therefore, if the restriction is released at the point, the following amount of elastic recovery must be observed:

$$\Delta \bar{E} = \bar{R}/\bar{\theta}$$

$$= \frac{(0.99\Omega Aa/A_s - 2\bar{\theta} \ln 10/Ab)}{(\Delta \bar{\theta})}$$

$$\sim -0.99\Omega/(\bar{\theta})$$

The last equality is obtained if the estimations

$$|\frac{\bar{\theta}}{Aa/Ab}| \ll 1, \quad \Delta K_a = 2 \ln 10/Aa \bar{b} \sim 10^1 \text{ [MPa]}, \quad \Omega = 10^1 \text{ [MPa]}$$

are taken into account. Equation (34) reveals that the residual strain $\eta$, which is calculated to be $|\Delta \bar{E}|$ [cf. Fig. 1(b)], is fully recovered after the process discussed here.

The case $\bar{\theta} > \bar{\theta}$ is interesting to examine. The thermomechanical behavior during the whole process is illustrated in Fig. 5. The reverse transformation stops on its way at the point $a$ at which the temperature $\bar{\theta}$ is reached. The recoverable force $K_a$ and the fraction $\xi_a$ at the point can be calculated by means of eqn (32). If the restriction is released at $a$ under the isothermal condition, the stress drops to zero along $abc$, and the strain recovery is associated as shown in the figure. The stress decrease along $ab$ promotes the reverse transformation, and the fraction progresses from $\xi_a$ to $\xi_b = 0.01$. During this process we observe the strain recovery which is equal to
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\[ E_{ab} = (0.01 - \xi_a)\Omega/\bar{D} \]  

(35)

Along the process bc a further strain recovery, which is due to the elastic unloading in the austenite, follows. Thus,

\[ E_{bc} = K_b/\bar{D} = (\lambda_a/\lambda \bar{b})(\theta - A_s)/\bar{D} - 2\ln 10/(\lambda \lambda b \bar{D}) \]  

(36)

**Numerical illustration**

In this section the uniaxial behavior of the polycrystalline shape memory alloy is shown to be well simulated by the theory developed in the preceding sections.

For the material constants listed in Table 1, which are determined from the experimental data reported by Poës [1970] for the Cu-Zn-Sn alloy, using eqns (22) and (24) a transformation strip in the stress-temperature plane is drawn in Fig. 6 representing a stress-induced martensitic transformation; a transformation strip for the reverse transformation is obtained using eqns (28) and (29). The transformation points are chosen as follows: \( M_f = -34^\circ C, M_s = -27^\circ C, A_s = -25^\circ C \) and \( A_f = -14^\circ C \). As \( \lambda \lambda b \) and \( \lambda \lambda \bar{b} \) are constant in this case, \( \Delta K_M = 10.5 \text{ MPa} \) and \( \Delta K_A = 16.5 \text{ MPa} \) follow from eqns (25) and (30). In other words, the width of the transformation strips remains constant at every temperature level.

Figure 7 contains the stress-strain curves determined by using the theory at several temperature levels. The stress-strain curve at \( \theta = -10^\circ C \) [Fig. 7(a)] clearly displays the pseudoelastic behavior above the point \( A_f \) [cf Fig. 3(a)]. It is worth noting that the value \( dK/d\varepsilon \), which corresponds to the strain-hardening parameter in plasticity, increases with the progress of transformation both in the loading and the unloading processes. The stress-strain curve at the point \( A_f \) is drawn in Fig. 7(b). As understood

<table>
<thead>
<tr>
<th>Material constants</th>
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<tbody>
<tr>
<td>MPa</td>
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<tr>
<td>---</td>
</tr>
<tr>
<td>( \bar{D} )</td>
</tr>
<tr>
<td>( 7 \times 10^4 )</td>
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</tbody>
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Fig. 6. Transformation strips
from Fig. 6, the reverse transformation is completed just when the stress unloads to zero. Comparison of Figs. 7(c) and 7(d) with Figs. 3(b) and 3(c) also shows that the theory can describe the behavior of the stress-induced martensite in the temperature range between the points \( A_f \) and \( M_s \).

According to Fig. 7(d), 0.99% of unrecoverable strain is observed after a successive loading and unloading process at \( \theta = -25^\circ \text{C} \). Figure 8 illustrates the stress variation induced in the specimen in the following process: The specimen is first heated up to a final temperature \( \theta \) while the deformation is restricted, and then the restriction is released when \( \vartheta \) is reached. The curve \( \vartheta = \bar{\vartheta} \) in the figure represents the case in which the reverse transformation is completed at the end of heating process. The temperature \( \bar{\vartheta} \) and corresponding stress \( \bar{K} \) are determined by use of eqn (33) to be
The subsequent linear relation of $K$ and $E$ means an isothermal elastic unloading of the austenite when the constraint is released at $\theta$. In the case of $\theta = 20$, $10$ or $0^\circ C$, the fraction of martensite phase is $0.106$, $0.28$ or $0.477$, respectively, during the heating process up to $\theta$. The remaining transformation then follows and is completed in the subsequent unconstrained process. Non-linear part of the curves describes this stage. Some amount of the unrecoverable strain is still observed after the whole process (around $0.05\%$ in all cases, cf. Fig. 8). Numerical calculation reveals that this disappears when the thermal expansion is negligibly small.

The progress of the reverse transformation is shown in $K$-$\theta$ plane of Fig. 9. It should be noted that the figure can be reread as the temperature-dependence of the recoverable force.

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