Stress-Strain-Temperature Relationship Associated with the R-Phase Transformation in TiNi Shape Memory Alloy* (Influence of Shape Memory Processing Temperature)

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The stress-strain-temperature relationship associated with the R-phase transformation in TiNi shape memory alloy is investigated experimentally and theoretically. The main results are summarized as follows. (1) The R-phase transformation showing a clear yielding stage in the stress-strain-temperature relationship appears at a certain shape memory processing temperature. (2) The R-phase transformation strip and the reverse transformation strip on the stress-temperature plane, which specify the characteristics due to the R-phase transformation are almost overlapping. Both transformation strips are narrow at high shape memory processing temperature. (3) The constitutive equation considering the volume fraction of the R-phase well describes the deformation behavior, such as the shape memory effect, pseudoelasticity and partial pseudoelasticity.

Key Words: Inelasticity, Nonferrous Metal, Titanium-Nickel Shape Memory Alloy, Rhombohedral Phase Transformation, Stress-Strain-Temperature Relationship, Shape Memory Processing Temperature

1. Introduction

In a TiNi shape memory alloy (SMA), the martensitic transformation (MT) and the rhombohedral phase transformation (RPT) occur⁽¹⁾⁻⁽³⁾. The strain range due to MT is about 5%, and that due to RPT about 0.5%. Because the hysteresis loop associated with the RPT is narrow and the fatigue life is long^{(4),(5)}, the applications of materials exhibiting the RPT are drawing attention.

For the application of SMA elements, recovery force or recovery deformation is used. In designing an

SMA element, the starting and completing temperatures of the motion, working stroke, initial deflection and initial load are established. In order to rationally establish these characteristic values, the stress-strain-temperature relationship of the material is necessary. Due to the dependence on stress, strain and temperature of the shape memory effect, pseudoelasticity and partial pseudoelasticity due to the RPT, the deformation behavior of the material is very complex. To date, the stress-strain-temperature relationship has been little reported.

In this paper, following the previous paper on the RPT⁽⁶⁾, we will discuss the stress-strain-temperature relationship of the material. Experiments of uniaxial tension on a TiNi SMA wire with various shape memory processing (SMP) temperatures will be described. We will expand the theory⁽⁷⁾⁻⁽¹¹⁾ proposed by the authors, in which the volume fraction of an induced phase is used as an internal state variable to describe the stress-strain-temperature relationship of the material. Furthermore, as the basic properties of the material, we will measure and discuss the transformation temperatures.

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2. Stress-Strain-Temperature Relationship

We assume that the uniaxial thermomechanical behavior of the material associated with the RPT can be governed by a set of equations, which are the same as those for the MT⁽⁷⁾⁻⁽¹¹⁾,

$$\dot{\sigma} = D' \dot{\varepsilon} + \Theta' \dot{T} + \Omega' \dot{\eta}, \quad (1)$$

$$\eta = H(\sigma, T), \quad (2)$$

where σ , ε and T represent the stress, strain and temperature, respectively, and the dot denotes the time derivative. The internal state variable η ($0 \leq \eta \leq 1$) represents the volume fraction of the rhombohedral phase (R-phase). The volume fraction of the parent phase is therefore $1 - \eta$. The coefficients D' and Θ' represent the modulus of elasticity and the thermoelastic constant, respectively. The quantity $|\Omega'/D'|$ represents the transformation strain range, which denotes the maximum recoverable strain and can be evaluated from the crystallographic difference between the austenite phase and the R-phase.

Because the transformation strain range $|\Omega'/D'|$ varies almost in proportion to T , we express $|\Omega'/D'|$ as a linear function of T . If D' is assumed constant, then Ω' is

$$\Omega' = mT + n. \quad (3)$$

Equation (1) describes the thermomechanical behavior of the material in the process of transformation. The progress of the transformation is governed by Eq. (2), which is called the transformation kinetics.

For the transformation kinetics of Eq. (2), we employ the following form, the same as the previous paper⁽⁶⁾.

$$\eta = -\{b'_M c'_M (M'_s - T) + b'_M \sigma\} \quad (4)$$

$$\eta = 1 + \{b'_A c'_A (A'_s - T) + b'_A \sigma\} \quad (5)$$

Equation (4) is applied to the RPT and Eq. (5) to the reverse transformation. M'_s and A'_s respectively represent the temperatures at which the RPT and the reverse transformation start under stress-free conditions. The coefficients b'_M , c'_M , b'_A and c'_A are the material constants.

From Eqs. (4) and (5), the respective starting and completing lines of the transformation are expressed as

$$\sigma = c'_M (T - M'_s), \quad (6)$$

$$\sigma = c'_M (T - M'_s) - 1/b'_M, \quad (7)$$

at $T \geq M'_s$ for the RPT and

$$\sigma = c'_A (T - A'_s), \quad (8)$$

$$\sigma = c'_A (T - A'_s) - 1/b'_A, \quad (9)$$

at $T \geq A'_s$ for the reverse transformation.

As found from these equations, if the coefficients b'_M , c'_M , b'_A and c'_A are constant, the transformation strips of the RPT and the reverse transformation are the regions located between two parallel straight lines. The RPT and the reverse transformation prog-

ress in the regions between the starting and completing lines of each transformation.

At the low temperatures of $T \leq M'_s$ and $T \leq A'_s$, the starting and completing stresses of the RPT and the reverse transformation are almost constant. Thus we assume that the respective starting and completing lines of the transformation are expressed as

$$\sigma = \sigma'_{M0} \quad (10)$$

$$\sigma = \sigma'_{M0} - 1/b'_M, \quad (11)$$

for the RPT and

$$\sigma = \sigma'_{A0}, \quad (12)$$

$$\sigma = \sigma'_{A0} - 1/b'_A, \quad (13)$$

for the reverse transformation.

The width of the transformation strip of the RPT is different above and below M'_s . Thus the coefficient b'_M is b'_{M1} at $T \leq M'_s$ and b'_{M2} at $T > M'_s$.

3. Experimental Method

3.1 Material

The material was Ti-55.2 wt% Ni SMA wire, 0.75 mm in diameter, which was fabricated by Furukawa Electric Co., Ltd. The wire was held at the SMP temperature, T_h , for 1 h before being cooled in the furnace so that it assumed a straight line. The values of T_h were set between 623 K and 773 K.

3.2 Experimental apparatus

The experimental apparatus was a shape memory property testing machine⁽⁶⁾ produced by Shimadzu Co. In this apparatus, axial force, displacement and temperature are controlled automatically. The specimen was heated by spraying compressed air heated by a heater and cooled by liquefied carbon dioxide. Axial force, displacement and temperature were measured with a load cell, an extensometer of 20 mm in gauge length and a thermocouple of 0.1 mm in diameter.

The transformation temperature of the specimen was measured with a differential scanning calorimeter (DSC-50) produced by Shimadzu Co.

3.3 Experimental procedure

The tensile tests were performed at a constant temperature T with a constant strain rate of 0.4%/min during the loading and unloading processes. The values of maximum strain ε_m were 0.6, 0.7 and 1%. The values of T were set at every 10 K between 303 K and 343 K. Variation in the temperature during each test was kept within ± 0.1 K.

The transformation temperature was measured according to the standard set by JIS H 7101.

4. Results and Discussion

4.1 Transformation temperature

The experimental results of the transformation temperature of the material at $T_h = 723$ K measured with the DSC are shown in Fig. 1. The transformation

temperatures are shown in Table 1, where M'_s , M'_f , M_s and M_f represent the starting and completing temperatures of the RPT and MT, respectively. A'_s , A'_f , A_s and A_f represent the respective starting and completing temperatures for the reverse transformation of RPT and MT. In Table 1, the transformation temperatures which are not clearly determined are left blank. As seen in Table 1, values of M'_s and M'_f decrease and those of M_s and M_f increase with a rise in SMP temperature T_h . The degree of variation in M'_s and M'_f with T_h is smaller than that in M_s and M_f . A'_s , A_s and A_f depend only slightly on T_h . Although values for A'_f

were not obtained, it is considered that A'_f is almost equal to A_f .

4.2 Stress-strain curves

Stress-strain curves obtained from tensile tests are shown in Fig. 2 as the fine lines for each test temperature T and SMP temperature T_h .

As seen in Fig. 2, at $T \leq A'_s$, the strain induced due to the RPT in the loading process remains after unloading. The residual strain disappears with heating under no-load conditions, which shows the shape memory effect. At $A'_s \leq T \leq A'_f$, part of the strain induced due to the RPT in the loading process disappears due to the reverse transformation during the unloading process, demonstrating partial pseudoelasticity. At $T \geq A'_f$, the strain induced due to the RPT in the loading process disappears due to the reverse transformation in the unloading process, showing pseudoelasticity.

As seen in Fig. 2, if T_h is low, at the same T the RPT stress is high and the slope of the curve during the RPT is large. This phenomenon is same as that for MT^{(12),(13)}. The reason why this phenomenon occurs may be considered as follows. If T_h is low, the large number of dislocations with high density which are

Fig. 1 Transformation temperatures measured with DSC ($T_h=723\text{K}$)

Table 1 Transformation temperatures of specimens (K)

T_h	M'_s	M'_f	M_s	M_f	A'_s	A'_f	A_s	A_f
623	332	312			309		298	339
648	328	311			315		296	337
673	325	312	247		316		295	334
698	320	309	255	221	316		299	330
723	319	307	256	228	315		303	329
773	319	298	276	261	315			333

Fig. 2 Stress-strain curves (thin lines for experimental results and thick lines for calculated results)

induced during the process of wire production through cold drawing remain after SMP⁽¹⁴⁾; thus the deformation resistance is high during the RPT.

In the case of high SMP temperature ($T_h = 773$ K), a horizontal yielding stage due to the RPT does not clearly appear at $T \leq A'_s$, and the MT starts at the strain of about 0.4% at $T = 343$ K. The reason why the RPT does not clearly appear at high T_h is that if T_h is high, the stress required to induce MT is low^{(12),(13)} and thus the RPT region is small.

4.3 Stress-strain-temperature relationships

The stress-strain-temperature relationships are shown in Fig. 3 as stress-strain curves at each temperature T and stress-temperature curves for the same strain. In Fig. 3, we show only the loading process for each SMP temperature T_h .

As seen in Fig. 3, at $T \leq A'_s$ where the shape memory effect is observed, the RPT stress is almost

Fig. 3 Stress-strain-temperature relationships:

constant, and therefore a plateau exists in the range of small strain. At $T \geq A'_s$ where pseudoelasticity is observed, the RPT stress increases with a rise in temperature, and therefore a slope appears. Also, for a strain axis, a plateau in the RPT region and a slope in the work-hardening region after completion of the RPT are observed. If T_h is high, the plateau is horizontal and appears clearly at low stress.

4.4 Transformation line and transformation strip

In order to represent the transformation stress, a schematic stress-strain curve at $T \geq A'_f$ is shown in Fig. 4. In Fig. 4, $\sigma_{M's}$ and $\sigma_{M'f}$ represent the starting and completing stresses of the RPT and $\sigma_{A's}$ and $\sigma_{A'f}$ those of the reverse transformation, respectively. As seen in Fig. 4, each transformation stress is determined by the intersection of the straight lines which represent the elastic region, the transformation region and the work-hardening region.

From the stress-strain curves in Fig. 2, the transformation stresses $\sigma_{M's}$, $\sigma_{M'f}$, $\sigma_{A's}$ and $\sigma_{A'f}$ are determined, and the relationship between them and temperature T is shown in Fig. 5 for each SMP temperature T_h .

As seen in Fig. 5, $\sigma_{M's}$ and $\sigma_{A's}$ are almost constant at $T \leq M'_s$ and increase almost in proportion to T at $T \geq M'_s$. At $T \geq A'_s$ the reverse transformation appears, and $\sigma_{A's}$ and $\sigma_{A'f}$ increase in proportion to T .

Each transformation strip is located between the starting line and the completing line of each transformation. As seen in Fig. 5, the RPT strip overlaps almost completely with the reverse transformation strip. This point corresponds to the fact that the hysteresis loops in the stress-strain curve, the strain-temperature curve and the stress-temperature curve are very narrow. On the other hand, in the case of the MT, the MT strip and its reverse transformation strip are separated by about 300 MPa in stress and by about 40 K in temperature, hence these transformation strips do not overlap⁽¹⁵⁾.

Fig. 4 Schematic stress-strain curve

As seen in Fig. 5, if T_h is high, the RPT strip and its reverse transformation strip are narrow. This means that at high T_h both transformations progress under almost constant stress. The narrowness of the transformation strip indicates the fast response to heating and cooling.

4.5 Transformation strain range

From the stress-strain curves in Fig. 2, the RPT starting and completing strains ϵ'_{Ms} and ϵ'_{Mf} are determined and the relationship between the RPT strain range $\Delta\epsilon_R = \epsilon'_{Mf} - \epsilon'_{Ms}$ and temperature T is shown in Fig. 6 for each SMP temperature T_h .

As seen in Fig. 6, $\Delta\epsilon_R$ is largest for $T_h = 673$ K. The higher the T , the smaller the $\Delta\epsilon_R$. A decreasing rate of $\Delta\epsilon_R$ with T is large around A'_s . Thus the largest recovery strain may be obtained in the case of $T_h = 673$ K and low T in the loading process. The phenomenon that the RPT strain range decreases with an increase in T is opposite to that of the MT⁽¹²⁾.

4.6 Modulus of elasticity

From Fig. 2, the slopes of the stress-strain curves in the loading process are determined and the relationship between the modulus of elasticity of the parent phase (austenite phase) D_A and temperature T is shown in Fig. 7 for each SMP temperature T_h .

As seen in Fig. 7, at $T \leq A'_s$ D_A is almost constant at 20~40 GPa. At $A'_s \leq T \leq A'_f$ D_A increases almost in proportion to T . At $T \geq A'_f$ D_A is almost constant at 80 GPa.

If T_h is high, at $T \geq A'_s$ D_A increases significantly with a rise in T . This phenomenon may be due to the fact that if T_h is high, a small number of dislocations

with high density which are induced during the process of wire production through cold drawing remain after SMP⁽¹⁴⁾; thus the deformation resistance is small, yielding small D_A especially at low T . Therefore D_A varies significantly with T .

4.7 Strain energy

For the stress-strain curves shown in Fig. 2, the area surrounded by the loading curve and the unloading curve and the area under the unloading curve represent the dissipated strain energy E_d and the recoverable strain energy E_r for unit volume, respectively. The relationships between these strain energies and temperature T are shown in Fig. 8 for each SMP temperature T_h .

As seen in Fig. 8, at $T \geq A'_f$ E_d is very small. E_r increases with increasing T . These phenomena may be caused by the fact that if T is high, the RPT stress and the reverse transformation stress are high and both stresses take almost the same value.

On the whole, if T_h is high, E_d is small. This may be caused by the fact that if T_h is high, the RPT stress is low and the RPT strain range is small.

If T_h is low, E_r is large. This may be caused by the fact that if T_h is low, the RPT stress and the reverse transformation stress are high and the RPT strain range is large.

A comparison of E_r of TiNi SMA with that of normal metal is given as follows. In the linearly elastic region, $E_r = \sigma\epsilon/2$. Thus for mild steel with the yield stress $\sigma = 200$ MPa and the corresponding strain $\epsilon = 0.1\%$, $E_r = 0.1$ MJ/m³. From Fig. 8, it is found that E_r of TiNi SMA is much larger than E_r of normal

Fig. 5 Transformation lines and transformation strips

Fig. 6 Relationship between R-phase transformation strain range and temperature

Fig. 7 Relationship between modulus of elasticity and temperature

Table 2 Values of coefficients

T_h	D'	m	n	b'_{M1}	b'_{M2}	c'_M	b'_A	c'_A	M'_s	A'_s	σ'_{M0}	σ'_{A0}
K	GPa	$\frac{\text{MPa}}{\text{K}}$		$\frac{1}{\text{MPa}}$	$\frac{1}{\text{MPa}}$	$\frac{\text{MPa}}{\text{K}}$	$\frac{1}{\text{MPa}}$	$\frac{\text{MPa}}{\text{K}}$	K	K	MPa	MPa
623	70	8.26	-2849	-0.013	-0.007	14.2	0.006	16.2	326	317	40	90
648		7.14	-2562	-0.022	-0.008	17.9	0.007	18.2	327	320	36	55
673		8.40	-3024	-0.046	-0.010	17.9	0.009	18.5	325	320	36	25
698		7.98	-2849	-0.111	-0.024	16.4	0.022	19.1	317	319	32	7
723		8.19	-2870	-0.094	-0.028	15.0	0.025	18.2	317	318	20	3

Fig. 8 Dissipated strain energy and recoverable strain energy in relation to temperature

metal. Thus TiNi SMA can function as an excellent energy storage material⁽¹⁶⁾.

In a similar way, the elastic deformation of normal metal is linear and thus E_d is small. In contrast, E_d of TiNi SMA shown in Fig. 8 is very large. Thus it is ascertained that TiNi SMA can function as an excellent high-damping material^{(17),(18)}.

4.8 Comparison of experimental results and numerical results

In this section, the coefficients in the stress-strain-temperature relationship shown in section 2 are determined based on the experimental results, and the simulated stress-strain curves will be compared with the experimental results.

Values of the coefficients determined based on the stress-strain curves in Fig. 2 and the transformation lines in Fig. 5 are shown in Table 2 for each SMP temperature. These values were determined as follows.

The coefficients b'_M and b'_A are reciprocals of difference between the starting and completing stresses of the RPT and the reverse transformation, respectively. The coefficient b'_M is b'_{M1} at $T \leq M'_s$ and b'_{M2} at $T > M'_s$. The coefficients c'_M and c'_A are the

slopes of the RPT line and the reverse transformation line at $T \geq M'_s$ and $T \geq A'_s$ on the stress-temperature plane, respectively. The transformation temperatures M'_s and A'_s are the intersections between the starting line of the RPT and the reverse transformation and the temperature axis on the stress-temperature plane. The transformation stress σ'_{M0} is an average of the RPT starting stress at $T \leq M'_s$, and σ'_{A0} is an average of the reverse transformation starting stress at $T \leq A'_s$. The relationship between $\Delta\epsilon_R$ and T shown in Fig. 6 can be approximated by a straight line. The coefficients m and n are proportional coefficients of the relationship between $\Delta\epsilon' (= D' \cdot \Delta\epsilon_R)$ and T and of the intersection with the vertical axis, respectively. Although the modulus of elasticity D' depends on T_h , T and η , we assume that D' is constant as 70 GPa because we are describing the overall behavior of SMA using a simple model in this study. Furthermore, because the thermoelastic effect is small in the range treated in the present paper, we assume $\Theta' = 0$.

The stress-strain curves simulated based on Eqs. (1) and (2), together with the coefficients shown in Table 2, are represented in Fig. 2 by the thick curves. Comparing the thin curves with the thick curves in Fig. 2, we find that the calculated results quantitatively describe the overall stress-strain relationships; that is, the shape memory effect at low temperature, pseudoelasticity at high temperature, partial pseudoelasticity at a certain moderate temperature, increase in the transformation stresses with rise in T , decrease in the transformation strain ranges with rise in T , and variation in a slope of the stress-strain curve in the transformation region with T_h .

However, the phenomena that D' depends on T and takes different values in the parent phase and the R-phase are not well described. The phenomena can be described by expressing D' as a function of T and η .

5. Conclusions

The stress-strain-temperature relationship associated with the RPT in TiNi SMA is investigated experimentally and theoretically. The main results are summarized as follows.

(1) The RPT showing a clear yielding stage on the stress-strain-temperature relationship appears at a certain SMP temperature.

(2) The RPT strip and the reverse transformation strip on the stress-temperature plane, which specify the characteristics due to the RPT, are almost overlapping. Both transformation strips are narrow at high SMP temperature.

(3) The constitutive equation considering the volume fraction of the R-phase well describes the

deformation behavior, such as the shape memory effect, pseudoelasticity and partial pseudoelasticity.

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