THE R-PHASE TRANSFORMATION IN THE Ti-Ni SHAPE MEMORY ALLOY AND ITS APPLICATION

I. Ohkata*, H. Tamura**
*Medical Division, PIOLAX Inc., Yokohama, 240 Japan
**Yokohama Research Laboratories, The Furukawa Electric Co., Ltd., Yokohama, 220 Japan

ABSTRACT

We discuss a comprehensive design approach of Ti-Ni alloy coil springs and introduce a new application of the R-phase transformation. In order to attain high cyclic performance, one must understand the two relationships between design parameters and material characteristics and between material characteristics and cyclic performance. Metallurgical parameters and coil spring dimensions play an important role as design parameters in the former relationship. High cyclic performance of an actuator is closely related to the suppression of the monoclinic martensite. Transformation temperatures and their stress dependence is of primary importance as material characteristics in the latter relationship. A thermostatic mixing valve, which is the latest application of the R-phase transformation in Japan is then discussed as a new type of a shape memory alloy actuator. The R-phase transformation is employed to achieve not only a long cycle life but a linear operation with the set temperature to continuously control the mixing ratio of hot and cold water. This is achieved by changing the total length of the two-way actuator in a linear manner with the set temperature. The linear characteristic is satisfied between 35-50°C by optimizing thermomechanical treatment and the dimensions of Ti-Ni and biasing coil springs.

INTRODUCTION

The R-phase transformation in the Ti-Ni shape memory alloy exhibits a small temperature hysteresis and excellent fatigue property[1]. The transformation also completes in a narrow temperature range, which makes it suitable for a fairly high rate actuation. However, the R-phase transformation is sensitive to thermomechanical treatment, alloy composition including the addition of a third element and repeating thermal cycles[2]. In order to utilize the R-phase transformation efficiently, one must start an actuator design from controlling material characteristics including transformation behavior and stress dependence of transformation temperatures. Figure 1 shows how coil spring dimensions and metallurgical parameters including the composition and heat treatment play an important role in determining the cyclic performance of an actuator. The relationships have been intensively but separately studied between design parameters and material characteristics and between material characteristics and cyclic performance.

One purpose of this study is to comprehend how the design parameters are determined in order to attain a large number of cycles by discussing the two relationships. Since coil springs have been mostly employed in SMA applications, we focus our attention on the cyclic performance of Ti-Ni shape memory coil springs. Another purpose is to introduce a new water mixing valve which utilizes the R-phase transformation. Water mixing valves require continuous and gradual temperature control. We have succeeded in controlling the temperature range of the R-phase transformation and optimizing an actuator operation in terms of the operation temperature, linear temperature characteristic and long cycle life.

Mat. Res. Soc. Symp. Proc. Vol. 459 © 1997 Materials Research Society

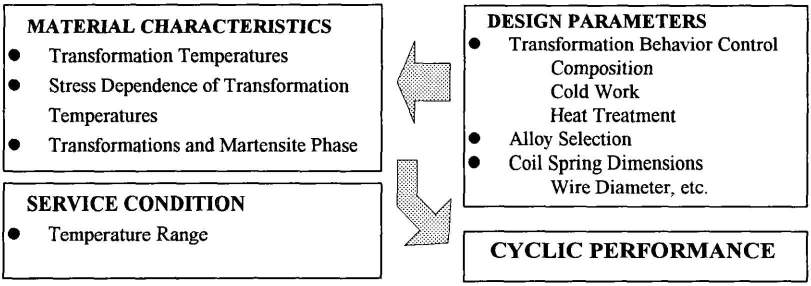

Figure 1 Comprehensive actuator design approach to achieve high cyclic performance. The approach links the two relationships between design parameters and material characteristics and between material characteristics and cyclic performance.

RELATIONSHIP BETWEEN MATERIAL CHARACTERISTICS AND CYCLIC PERFORMANCE

We consider intrinsic cyclic performance of different transformations, effect of the temperature range in a repeating thermal cycle and effect of strain.

Intrinsic Cyclic Performance of Different Transformations

Different cyclic performance is obtained depending on a martensitic phase and an alloy system. A coil spring exhibits poor cyclic performance as shown in Figure 2 when only the B2-monoclinic martensite transformation takes place in a repeating thermal cycle. On the other hand, a half million operation is reported for an actuator which utilizes the R-phase transformation[3]. However, the shape recovery strain is much smaller and about 1% for the latter case. Ti-Ni-Cu alloys with more than 8at% Cu substituted for Ni have an in-between shape memory property. The cyclic performance is typically over one million, less than one hundred and ten thousand cycles for the R-phase(Ti-Ni), B2-monoclinic martensite(Ti-Ni) and B2-orthorhombic martensite(Ti-Ni-Cu) transformations, respectively[4]. A required number of cycles and actuation stroke and degree of allowable temperature hysteresis in service usually determine which alloy system and transformation should be utilized.

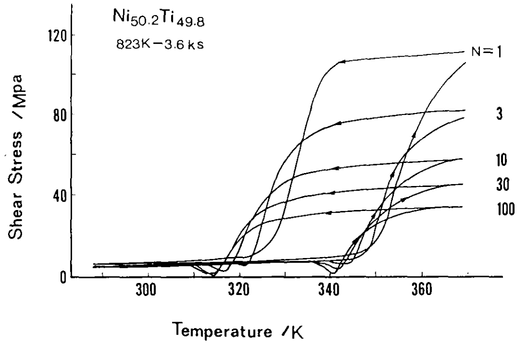

Figure 2 Cyclic performance of a Ti-50.2at%Ni coil spring which utilizes the B2-monoclinic martensite transformation. The spring is heat-treated at 823K for 3.6ks, and the shear stress is measured under 0.75% strain. N indicates the number of cycles.

Effect of Temperature Range in Repeating Thermal Cycle

The temperature range in service has primary importance because if service temperature decreases below the Ms temperature of a Ti-Ni alloy determined under zero stress, one cannot avoid the generation of the monoclinic martensite in service. Figure 3 compares the cyclic performance of a Ti-50.2at%Ni coil spring in three temperature ranges[5]. The Ms and Mf temperatures of the alloy is 294K and 282K, respectively. It is clear that the temperature-shear stress curve changes more remarkably with a decreasing lower temperature limit below Ms. The shape recovery force decreased by about 35% after 10^4 cycles when the lowest temperature was 4K below Ms((b)) and 65% when 4K below Mf((c)).

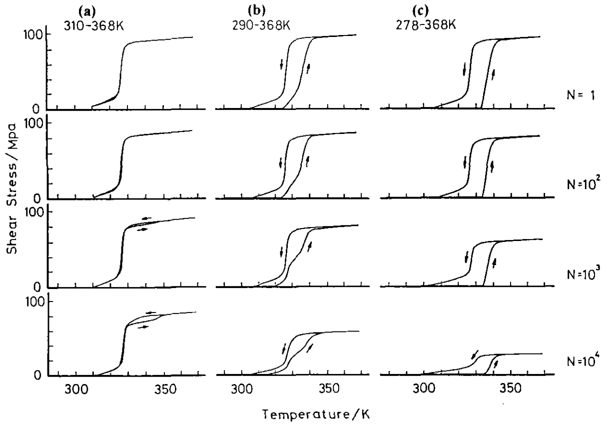

Figure 3 Cyclic performance of a Ti-50.2at%Ni coil spring in three different temperature ranges under 0.4% strain. The lowest temperature in cycles (b) and (c) is below Ms, which is 294K. N indicates the number of cycles.

A large separation of the R-phase and R-monoclinic martensite transformations is favored in order to assure that the lowest service temperature lies between Mf' and Ms. One can attain such control by appropriately choosing the alloy composition and thermomechanical treatment condition.

Effect of Strain

One must take account of the change in transformation temperatures under stress and

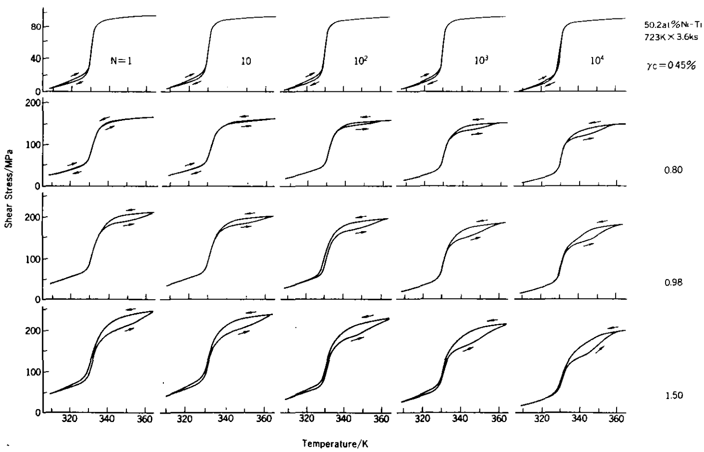

Figure 4 Effect of the constant strain(γ_c) on the cyclic performance of a Ti-50.2at%Ni coil spring. Springs were subjected to a repeating thermal cycle under four different γ_cs between 308K and 363K, which is above Ms=283K. N indicates the number of cycles.

strain. The operation temperature of an actuator can be therefore controlled by using a biasing spring. However, the cyclic performance remarkably degrades if the Ms temperature is increased above the lowest service temperature by stress. When a Ti-Ni coil spring is subjected to a repeating thermal cycle under a constant strain, its cyclic performance can be predicted from its initial temperature-stress characteristic[6]. Figure 4 shows the effect of the constant strain on the cyclic performance of a Ti-50.2at%Ni coil spring[7]. When the strain increases, a small hysteresis loop appears above the apparent Ms' temperatures in the first cycle. While the temperature-stress characteristic remains almost unchanged after 10^4 cycles if the initial curve does not exhibit the small hysteresis, the recovery force remarkably decreases when the small hysteresis appears in the initial curve. This indicates that a Ti-Ni coil spring has the critical strain below which the cyclic performance remains excellent.

We consider the critical strain is closely related to the generation of the stress-induced monoclinic martensite from the B2 phase. The stress dependence of the transformation temperatures is schematically shown in Figure 5[7]. When the constant strain is small and the stress at high temperatures does not exceed τ_X, which is the critical stress at which Ms and Ms' coincide, temperature-stress curve t_u-a-b-t_l-c-d-t_u is obtained. Only the R-phase and its reverse transformations are involved in this case. Segment t_u-b is sloped due to the change in the lattice parameters of the R-phase. When the constant strain is large and the stress at high temperatures becomes above τ_X, the temperature-stress curve is represented by T_u-A-B-C-T_l-D-E-F-T_u. When a coil spring is cooled down from T_u, the first transformation to occur is not the R-phase transformation but the B2-monoclinic martensite transformation at point A. The generation of the martensite then relaxes the strain, and when the stress reaches τ_X at point B, the remaining B2 phase transforms to the R-phase. We believe that the R-phase and monoclinic martensite coexist at point T_l. In the heating cycle, the R-phase and monoclinic martensite start reversely transforming to the B2 phase at point D and F, respectively.

The maximum stress in service should not exceed τ_X. This condition is usually achieved by appropriately determining coil spring dimensions including the wire diameter, mean diameter and number of effective turns. τ_X is a function of the alloy composition and thermomechanical treatment[8].

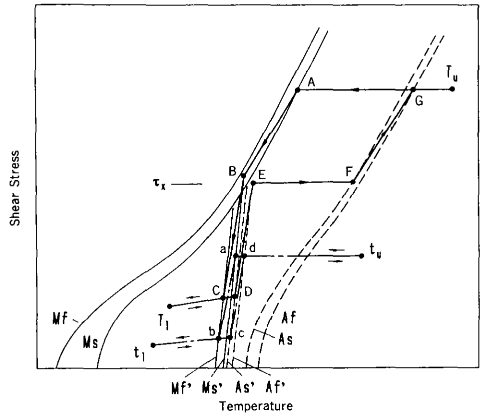

Figure 5 Schematic representation of two types of temperature-shear stress curves, t_u-a-b-t_l-c-d-t_u and T_u-A-B-C-T_l-D-E-F-G-T_u, with the stress dependence of transformation temperatures. The Ms' and Ms temperatures coincide at stress τ_x.

RELATIONSHIP BETWEEN DESIGN PARAMETERS AND MATERIAL CHARACTERISTICS

Transformation Behavior of Ti-Ni Alloys

The effect of the alloy composition and thermomechanical treatment has been intensively studied on the transformation behavior[9]. Figure 6 shows DSC curves of a work-hardened Ti-49.7at%Ni alloy as a function of the heat treatment temperature[10]. Each transformation temperature

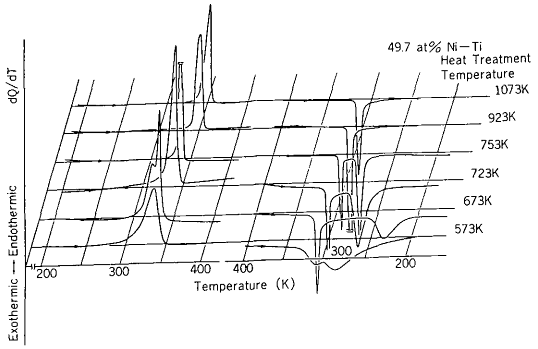

Figure 6 DSC curves for a Ti-49.7at%Ni alloy heat-treated at different temperatures indicated in the figure. The scan rate is 20K/min.

determined from the DSC curves is plotted in Figure 7. Work-hardened Ti-Ni alloys exhibit two transformations in cooling, that is, the R-phase and R-monoclinic martensite transformations when it is heat-treated below 773K[11]. The separation of the two transformations becomes larger for higher Ni-content alloys and largest for the heat treatment at around 673K. The addition of a third element to Ti-Ni alloys usually decreases the transformation temperatures[12] and brings about a larger separation of the two transformations[13].

Ms' and Mf' are not sensitive to the heat treatment temperature. The Ms' temperature gradually decreases with increasing heat treatment temperature, while Ms increases more rapidly when heat-treated above 673K. This implies that the separation of the two transformations becomes smaller for higher heat treatment temperature, which can result in the generation of the stress induced martensite and poor cyclic performance.

The transformation temperature range is also a function of the alloy composition and thermomechanical treatment condition. A wide temperature range implies a gentle operation of an actuator. Both the R-phase and R-monoclinic martensite transformations exhibit a wider transformation temperature range for lower heat treatment temperature. However, the dependence is much more significant for the R-monoclinic martensite transformation.

Stress Dependence of Transformation Temperatures

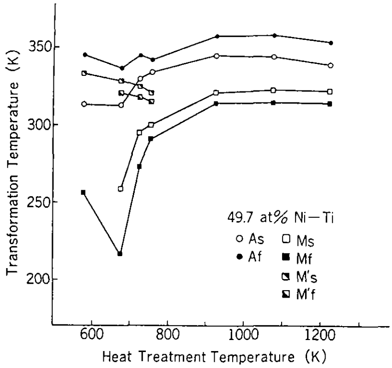

Figure 7 Transformation temperatures of a Ti-49.7at%Ni alloy determined from Figure 6 as a function of the heat treatment temperature.

It is important to know the change in the transformation temperatures with stress to secure the separation of the R-phase and R-monoclinic martensite transformations in service as well as to control the operation temperature of an actuator. The transformation temperatures increase under stress according to the Clausius-Clapeyron relationship. The stress dependence of the R-phase transformation temperatures is much smaller than that of the R-monoclinic martensite transformation reflecting smaller transformation strain and transformation heat of the former[8].

Ms and Ms' coincide at τ_x(Figure 5), and above this stress the generation of the monoclinic martensite accelerates the degradation of the recovery force. Coil spring dimensions should be so determined that the maximum stress in service does not exceed τ_X. The transformation temperatures and τ_X depend on the alloy composition and thermomechanical treatment. Therefore, the compilation of material characteristic data is indispensable for the actuator design as a function of the design parameters.

A NEW APPLICATION OF R-PHASE TRANSFORMATION - WATER MIXING VALVE

Background of Development

Figure 8 shows three conventional types of water mixing valves. In the double valve type((a)), water temperature is controlled by manually adjusting two valves for hot and cold water. The water mixing ratio can be controlled with one lever in the single lever type((b)). However, it is not always easy to realize desired water temperature in these two types. The water temperature fluctuates even during an apparent steady state use. The fluctuation is caused by the variation in the water pressure resulting from water discharge elsewhere in the waterline. The pressure increase and decrease brings about the temperature drop and rise, respectively. The thermostat type((c)) automatically controls the water mixing ratio by sensing the water temperature. The market share of the thermostat type has been increasing to about 40% in Japan.

The conventional thermostat type mostly employs a wax actuator. Figure 9 shows the structure of a thermostat type valve. When the water temperature exceeds the set temperature, the wax expands and the actuator moves the spool to left resulting in a decreased mixing ratio of hot and cold water. When the water temperature becomes lower, the spring contracts the wax, which increases the mixing ratio. The temperature control is thus automatically done.

The most critical problem with wax actuators is a slow thermal response. When one interrupt the water and open the valve again or when one quickly increases the set temperature, too hot water is sometimes discharged. This is caused by a poor thermal response and called overshoot. The structure of a wax actuator is shown in Figure 10. Paraffin wax is enclosed in a copper vessel with a rubber diaphragm fixed at one end. The actuator utilizes the volume expansion accompanying the solid-to-liquid transition of wax in heating. The overshoot is caused by slow thermal conduction and the delay in actual volume expansion of the paraffin wax.

Thermostatic Operation with SMA Actuator

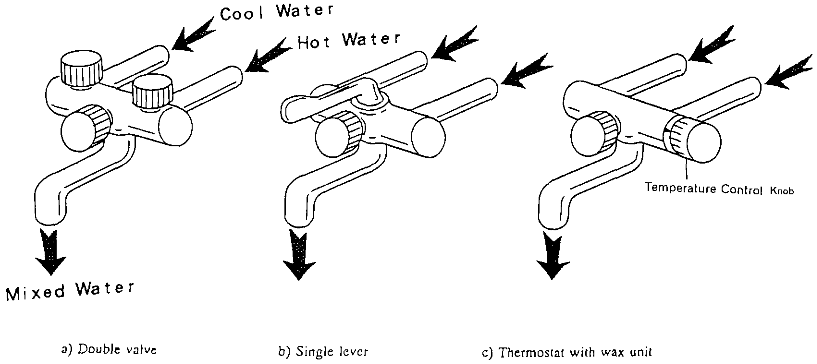

Figure 8 Three types of conventional water mixing valves

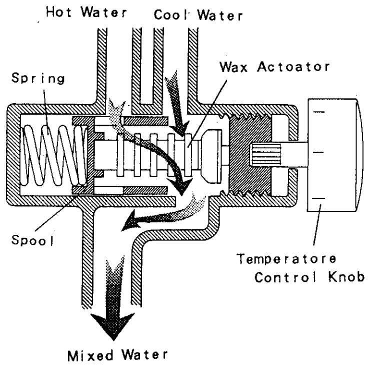

Figure 9 Structure of a conventional thermostat type valve using a wax actuator.

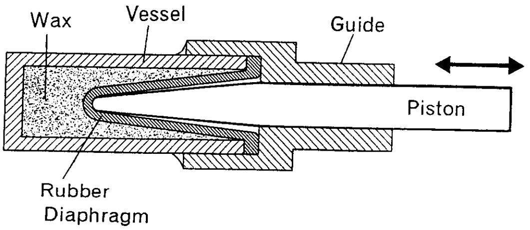

Figure 10 Cross section of a wax actuator

An excellent thermal response is expected for an SMA coil spring by directly exposing it to water. Figure 11 schematically compares the temperature-force characteristics under a constant deflection of a Ti-Ni coil spring and a wax actuator with an identical outer diameter. The force is much stronger for the Ti-Ni coil spring. A simpler mixing valve with a Ti-Ni coil spring can be designed with a better thermal response if one can attain small hysteresis and control the force with temperature.

Figure 12 schematically shows the new mixing valve with an SMA two-way actuator. The temperature control knob varies the total length of the actuator through the equi-pitched screw. Therefore, the total length of the actuator has a linear relationship with the set temperature. In order to control the water temperature, the spool must be shifted in a linear manner with the set temperature under equilibrium. We can prove that the R-phase transformation is well suited for such control as follows.

The linearity between the total actuator length(L_{tot}) and set temperature(T_{set}) is given by:

$$\Delta L_{tot} = \alpha \bullet \Delta T_{set} \tag{1}$$

where Δ and α denote a change in an amount from an initial state and a constant, respectively. With spring constant K_b and deflection δ_b, the biasing force is given as $K_b \bullet \delta_b$. We approximate the force of a Ti-Ni coil spring at temperatures between Ms' and Mf' as $(K_{s0}+\beta \bullet \Delta T_{act}) \bullet \delta_s$, where K_{s0} and δ_s denote a constant and the deflection of a Ti-Ni coil spring, respectively. β represents the temperature dependence of the spring constant. ΔT_{act} is the change in actual water temperature. At equilibrium, the two forces must be equal:

$$K_b \bullet \delta_b = \left(K_{s0} + \beta \bullet \Delta T_{act}\right) \bullet \delta_s \tag{2}$$

or

$$K_b \bullet \Delta\delta_b = K_{s0} \bullet \Delta\delta_s + \beta \bullet \Delta T_{act} \bullet \delta_s \tag{2'}$$

L_{tot}, δ_b and δ_s follow:

$$\Delta L_{tot} + \Delta\delta_b + \Delta\delta_s = 0 \qquad (3)$$

The relationship between $\Delta\delta_s$ and ΔT_{act} is determined by a valve structure and, with γ being a constant, given by

$$\Delta T_{act} = \gamma \bullet \Delta\delta_s \qquad (4)$$

From (1), (2'), (3) and (4), the following relationship is derived between ΔT_{set} and $\Delta\delta_s$:

$$K_b \bullet \alpha \bullet \Delta T_{set} + \left(K_b + K_{s0} + \beta \bullet \gamma \bullet \delta_s\right) \bullet \Delta\delta_s = 0 \qquad (5)$$

When $\Delta\delta_s$ is much smaller than δ_{s0}, which is the deflection of a Ti-Ni coil spring in the initial state, the linearity between ΔT_{set} and $\Delta\delta_s$ is established as:

$$K_b \bullet \alpha \bullet \Delta T_{set} + \left(K_b + K_{s0} + \beta \bullet \gamma \bullet \delta_{s0}\right) \bullet \Delta\delta_s = 0 \qquad (6)$$

Note that $\Delta\delta_s$ represents the spool displacement in Figure 12. Therefore, the spool displacement can be controlled in a linear manner with the set temperature by varying the total actuator length as in (1).

It is essential to control the temperature dependence of the spring constant during the R-phase transformation. If the transformation is gentler with temperature, the above expression for the force of a Ti-Ni coil spring holds in a wider temperature range, and a linear spool displacement and water temperature control can be obtained therein. In conventional wax actuators, the temperature dependence of force is controlled by mixing two waxes with different melting temperatures.

SMA actuators so far utilize the difference in deflections or forces below M_f' and above A_f'. The new mixing valve utilizes the linear relationship between the temperature and force during the R-phase transformation for the first time. The temperature dependence is controlled by the design parameters described earlier, that is, the alloy composition, thermomechanical treatment conditions including heat treatment temperature and cold working ratio and dimensions of Ti-Ni and biasing coil springs. Based upon fundamental data on the relationships between these parameters and the temperature dependence, we have succeeded in obtaining linear control in the 35 to 50°C range as well as excellent cyclic performance utilizing the R-phase transformation (Figure 13).

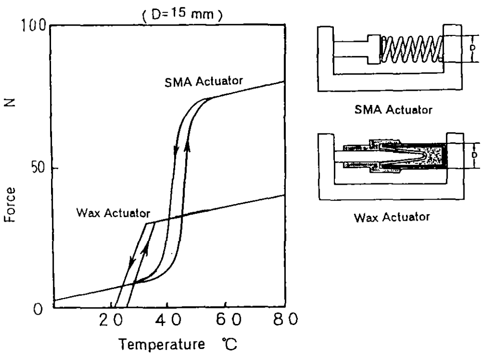

Figure 11 Temperature-force characteristics of SMA and wax actuators with an identical outer diameter, D(schematic).

New Water Mixing Valve[14]

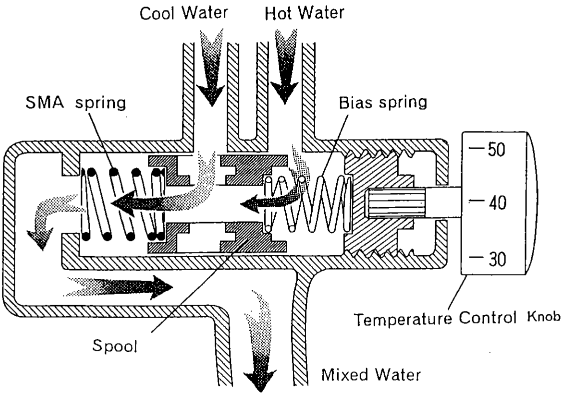

Figure 12 Structure of the new mixing valve using SMA and biasing coil springs. The spool position and the mixed water temperature is controlled by varying the total length of the actuator linearly with the set temperature by the control knob. A linear temperature-deflection(force) characteristic in a wide temperature range is imparted to the SMA spring by optimizing the alloy composition and thermomechanical treatment condition.

Figure 14 exhibits the new water mixing valve. The Ti-Ni coil spring directly contacts the mixed water in Figure 12 and has a good thermal response. The water temperature is set by the temperature control knob as in the conventional thermostat valve. The knob changes the total length of the actuator, the biasing force and the spool position. The temperature fluctuation can be compensated as follows. When the actual water temperature becomes higher than the set temperature, the SMA spring pushes the spool to right, which in turn results in a decreased fraction of hot water and the recovery to the set temperature. When the actual temperature fluctuates lower, the opposite mechanism works.

Figure 15 compares the thermal response of the new and conventional valves. The set temperature is 42°C, and the temperature fluctuation was measured after one minute interrupt of discharge. For the conventional valve with a wax actuator, the water temperature fluctuates by about ten degrees from 38°C to 47°C and is stabilized at 42°C. The fluctuation range is smaller than two degrees for the new valve, which is not distinctly sensed by people.

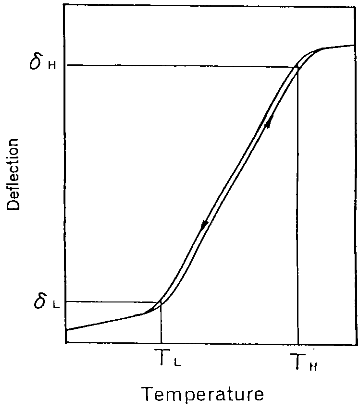

Figure 13 Schematic representation of the temperature-deflection characteristic of the linear shape memory component used in the new mixing valve. The characteristic exhibits linearity between (temperature, deflection)=(T_L, δ_L) and (T_H, δ_H).

CONCLUSION

We have demonstrated that the R-phase transformation in the Ti-Ni alloy can be utilized for linear temperature control with a large number of operation cycles. The optimization of SMA actuators requires the link of the two relationships between design parameters and

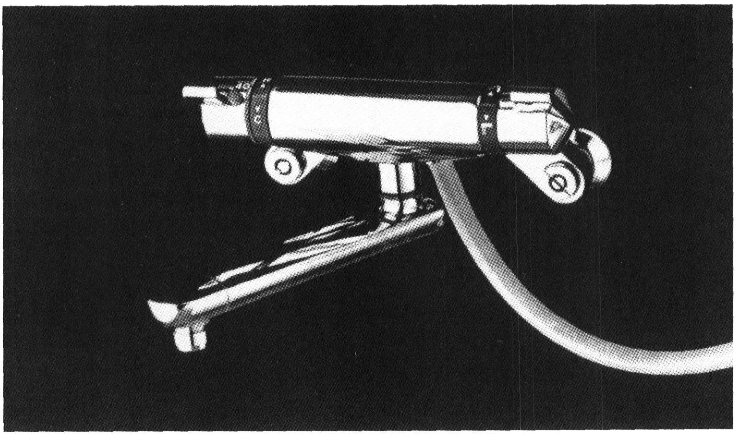

Figure 14 Appearance of the new mixing valve using the linear shape memory component (courtesy of TOTO Ltd.).

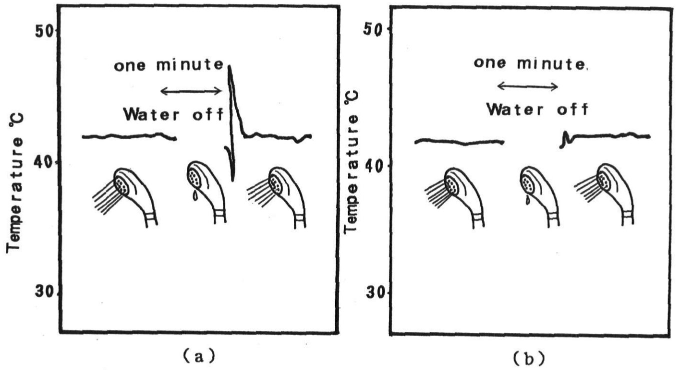

Figure 15 Comparison of the thermal response of a conventional thermostat type valve(a) and the new mixing valve(b). 42°C water is interrupted for one minute, and then the valve is re-opened.

material characteristics and between material characteristics and cyclic performance. An addition of a new function like the linear temperature control also becomes possible by the same approach.

REFERENCES

1. H. Tamura, Y. Suzuki and T. Todoroki, Proc. Int. Conf. on Martensitic Transformations, Japan Inst. Metals, p.736(1986).

2. S. Miyazaki and K. Otsuka, Phil. Mag. A, **50**, p.393(1984).

3. Y. Suzuki, J. Rob. Mech., **1**, p.240(1989).

4. Y. Tsuzuki and H. Horikawa, Furukawa Rev., **9**, p.18(1991).

5. H. Tamura, K. Mitose and Y. Suzuki, J. DE PHYS. Ⅳ, Colloque C8, supplément au J. de Phys. Ⅲ, **5**, C8-617(1995).

6. Y. Suzuki and H. Horikawa, Mat. Res. Soc. Symp. Proc., **246**, p.389(1992).

7. H. Tamura, Furukawa Rev., **6**, p.123(1988).

8. T. Todoroki and H. Tamura, J. Japan. Inst. Metals, **50**, p.538(1986) (in Japanese).

9. T. Todoroki and H. Tamura, Trans. Japan Inst. Metals, **28**, p.83(1987).

10. H. Tamura and Y. Suzuki, Furukawa Rev., **4**, p.33(1986).

11. S. Miyazaki, Y. Ohmi, K. Otsuka and Y. Suzuki, J. DE PHYS., Colloque C4, supplément au n° 12, Tome 43, C4-255(1982).

12. K.H. Eckelmeyer, Scripta Met., 10,p.667(1976).

13. C.M. Hwang, M. Meichle, M.B. Salamon and C.M. Wayman, Phil. Mag. A, **47**, p.9(1983).

14. H. Matsui, M. Enoki, T. Kato, J. DE PHYS. Ⅳ, Colloque C8, supplément au J. de Phys. Ⅲ, **5**, C8-1253(1995).