

Shape memory alloys – characterization techniques

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Abstract. Shape memory alloys are the generic class of alloys that show both thermal and mechanical memory. The basic physics involved in the shape memory effect is the reversible thermoelastic martensitic transformation. In general, there exists two phases in shape memory alloys, viz., a high-temperature phase or austenitic phase (A) and a low-temperature phase or martensitic phase (M). In addition, an intermediate R phase exists in some special cases. The $M \leftrightarrow A$ transformation is associated with a recoverable strain of about 6.5–8% and the $R \leftrightarrow A$ transformation is associated with a recoverable strain of about 1%. The former transformation has been widely used in the applications like antenna deployment of satellite, aerospace couplings, orthodontic arch wires, medical guide wires for diagnostic and therapeutic catheters and other industrial applications. Our group has been giving emphasis to the characterization techniques for R phase, using differential scanning calorimetry (DSC), electrical resistivity probe (ER) and thermomechanical analyzer (TMA). R phase is found to have attractive features like stability against thermal cycling, a small thermal hysteresis and a negligible strain recovery fatigue. DSC has been used successfully to characterize the recoverable strain parameters, apart from the determination of transformation temperatures. ER is used, for the systematic study of the dependence of various phases on heat-treatment temperatures. TMA has been effectively employed for the study of the mixed phases. A space-rotating platform is designed and fabricated, using an actuator of shape memory spring, for obtaining controlled rotations. The efficiency and the reliability of this actuator has been tested, over a million thermal cycles.

Keywords. Shape memory alloys; characterization techniques; austenitic phase; martensitic phase; R-phase.

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1. Introduction

Shape memory alloys (SMA) are the class of alloys that exhibits both thermal and mechanical memory. The shape memory effect (SME) was first observed in gold–cadmium alloy in 1932. The effect has been observed in many alloy systems, such as Cu–Zn, Cu–Zn–Al, Cu–Zn–Ga, Cu–Zn–Sn, Cu–Zn–Si, Fe–Pt, Ni–Ti etc. At high temperature SMAs exhibit pseudoelastic (PE) behavior. They can recover a large amount of strain of the order of 8% on loading and unloading. Both SME and PE properties of shape memory alloys have extensive applications. Of the different alloys that display the shape memory effect, only

only NiTi- and Cu-based alloys have proven commercially viable with useful engineering properties [1].

The shape memory effect is a phenomenon which involves thermoelastic reversible crystallographic phase transformation from a high-temperature phase to a low-temperature phase. In Nitinol, high-temperature phase has bcc crystal structure and low-temperature phase has monoclinic phase. In addition to these two phases there is one more intermediate phase known as the R phase which has the rhombohedral crystal structure, appearing in some special cases. In such cases, the direct transformation is a two-stage process, the material at high temperature in the parent phase (A) transforms to the intermediate phase (R) and then to the low temperature or product phase (M) [2–4]. The recoverable strain associated with the R phase is very small, of the order of 0.5%, when compared to that of the martensitic transformation where it is of the order of 6.5%–8.5%. However, the R phase has some attractive properties, like stability to thermal cycling and ageing, very small thermal hysteresis and very high fatigue life, etc. [5].

The study of crystalline phase transformation behavior involves many techniques, viz., differential scanning calorimetry, electrical resistivity, thermal expansion, internal friction measurement and thermoelectric power. Using these probes, transformation behavior has been studied extensively by many researchers [6–11]. The present author has used differential scanning calorimeter (DSC) for the study of transformation temperature and recoverable strain which are the two main design parameters in applications. Electrical resistivity probe has been used for systematic study of dependence of various phases on heat-treatment temperature and stability against thermal cycling. Thermomechanical analyzer (TMA) has been used to study the mixture of R and M phases. A prototype of thermal actuator is designed and fabricated in-house using a two-way shape memory spring, and has been tested over a million thermal cycles for its reliability and efficiency.

2. Experimental

The near equiatomic prior cold worked (40%) Nitinol in the form of wires of diameters 1 mm and 2.4 mm used in this investigation are obtained from Special Metals Corporation, USA. The samples are annealed for 20 min at the desired high temperatures in a muffle furnace and then quenched into water at room temperature. The samples are heat treated at different temperatures starting from 300°C to 800°C. For the thermal study of the samples, a DSC (Shimadzu DSC-50) has been employed. In this investigation, a constant rate of heating and cooling has been maintained at 2°C/min. For the study of thermal expansion, a TMA (Shimadzu TMA-50) has been used and both DSC and TMA have been interfaced to a computer through a thermal analyzer (Shimadzu TA-50). For the electrical resistivity measurements, a home-made four-probe setup is used. Digital multimeters have been used to measure the voltage developed across the two probes and the constant current through the sample, 10 μ V and 100 μ A being the precision of voltage and current measurements, respectively. The resistivity measurements are carried out in the temperature range from 30°C to 120°C during both heating and cooling cycles and the rate of heating/cooling is maintained at 3°C/min.

3. Results and discussions

3.1 DSC characterization

DSC is the most widely used technique to determine the transformation temperatures and to get the energy of transformations of shape memory alloys. The heat treatment is of general interest in shape memory alloys as various phases in these alloys depend upon heat-treatment temperatures. We have used the DSC to characterize the systematic dependence of various phases of NiTi on heat-treatment temperature [6]. The existence of R phase, in particular, plays a key role in determining the shape memory properties like recoverable strain and the stability against thermal cycling which are some of the important engineering parameters. Two kinds of samples are chosen for the study of the effect of linear strain on shape memory properties, one heat-treated at 560°C in which only martensitic phase exists at room temperature, and the other heat-treated at 340°C in which there exists a mixture of R and M phase at room temperature. The heat-treated samples are subjected to a linear strain by applying a tensile stress. The wire samples are subjected to linear strains in the range 0–30%. The sample heat-treated at 340°C was found to withstand maximum strain of only 14% due to the inherent stiffness.

Figures 1a and 1b show the DSC thermograms of samples heat-treated at 560°C and 340°C, respectively. The increase in the transformation temperatures and the decrease in the width of transformation can be clearly seen for the samples strained up to 8% in the case of sample heat-treated at 560°C. Thereafter, the width again increases. The asymmetry

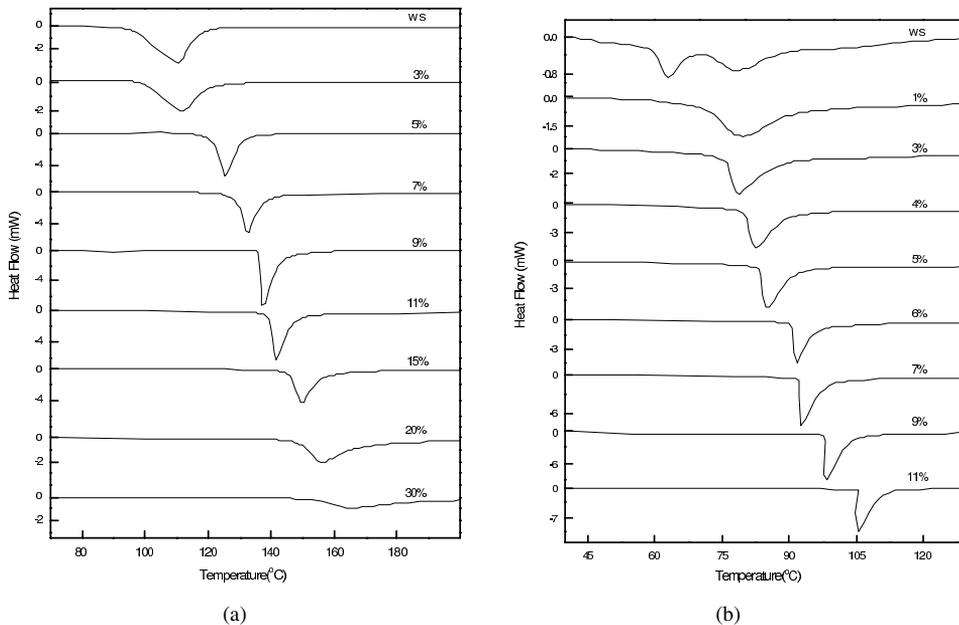


Figure 1. DSC thermograms at different strains obtained during heating part of the cycle for Nitinol. (a) Heat-treated at 560°C and (b) heat-treated at 340°C.

of endothermic peak around peak temperature T_p is maximum for the sample heat-treated at 9%. In the case of the sample heat-treated at 340°C, the unstrained sample consists of two phases, R and M, as indicated by the peak splitting of the endotherm. But straining the sample to 1% shows the disappearance of the R phase. The transformation temperatures, energy of transformation and asymmetry of the endothermic peak of these samples are given in table 1.

In general, for the recovery of a given strain, SMA must have small thermal width of $M \rightarrow A$ transformation, low energy of transformation and more or less symmetric endotherm peak. Asymmetry in the endotherm peak can be known by comparing the values of $T_p - A_s$ and $A_f - T_p$ listed in table 1. For the sample heat-treated at 560°C and strained at 9% the endotherm peak becomes highly asymmetric. Therefore, it can be concluded that Nitinol wire can have a maximum recovery if the applied strain is below 9%. In the case of the samples heat-treated at 340°C maximum recovery is possible if the strain is below 7%. Details of the analysis leading to this conclusion are given in ref. [12].

3.2 ER characterization

Electrical resistivity is a function of crystal structure. Shape memory alloys have different crystal structures in different phases like bcc in high temperature austenitic phase, monoclinic in low temperature martensitic phase and rhombohedral in R phase, for a NiTi alloy. The temperature dependence of the resistivity shows a sudden increase while going from martensitic phase to austenitic phase and a sudden decrease while going from austenitic

Table 1. Dependence of energy of transformation, thermal width of transformation and asymmetry on the applied linear strain in the case of Nitinol heat-treated at 560°C and 340°C.

| Sample | Heat treated at 560°C | | | | Heat treated at 340°C | | | |
|----------------|-----------------------|------------------|------------------|------------------|-----------------------|------------------|------------------|------------------|
| | Energy (J/g) | $T_p - A_s$ (°C) | $A_f - T_p$ (°C) | $A_f - A_s$ (°C) | Energy (J/g) | $T_p - A_s$ (°C) | $A_f - T_p$ (°C) | $A_f - A_s$ (°C) |
| Without strain | -19.01 | 18.9 | 11.6 | 30.5 | - 8.71 | - | - | - |
| 1% strain | - | - | - | - | -12.72 | 14.8 | 12.7 | 27.5 |
| 3% strain | -13.10 | 16.2 | 12.7 | 28.9 | -14.81 | 7.0 | 13.0 | 20.0 |
| 4% strain | - | - | - | - | -11.82 | 4.2 | 11.6 | 15.8 |
| 5% strain | -15.59 | 9.0 | 9.1 | 18.1 | -11.67 | 2.4 | 10.0 | 12.4 |
| 6% strain | - | - | - | - | -11.77 | 1.8 | 7.5 | 9.3 |
| 7% strain | -16.03 | 8.2 | 8.3 | 16.5 | -14.06 | 0.3 | 8.5 | 8.8 |
| 8% strain | -18.08 | 6.6 | 8.2 | 14.8 | - | - | - | - |
| 9% strain | -19.05 | 2.8 | 12.8 | 15.6 | -14.41 | 1.9 | 8.1 | 10.0 |
| 11% strain | -18.75 | 6.4 | 9.8 | 16.2 | -14.01 | 0.6 | 8.5 | 9.1 |
| 13% strain | -17.34 | 6.6 | 13.2 | 19.8 | - | - | - | - |
| 15% strain | -15.72 | 8.3 | 13.8 | 22.1 | - | - | - | - |
| 20% strain | -14.05 | 13.7 | 24.9 | 38.6 | - | - | - | - |

phase to martensitic phase. The R phase has the highest resistivity value and its existence is observed by the appearance of peak in resistivity vs. temperature curve.

The results of the resistivity measurements are shown in figures 2a and 2b for heating and cooling parts of the cycles, respectively. Untreated sample has a high resistivity of $126 \mu\Omega \text{ cm}$ at 30°C , possibly due to the presence of a large number of point defects and dislocations as it is highly cold-worked. The heat-treatment process leads to the decrease in strain and crystalline defects in cold-worked sample [13]. Therefore, the resistivity is expected to decrease with increase in heat-treatment temperature. It is also observed that around 60°C , temperature coefficient of resistance (TCR) of the sample continuously decreases from positive value at lower heat-treatment temperature to negative value at higher heat-treatment temperature up to certain limiting value of heat-treatment temperatures. This is due to the formation of R phase with increase in heat-treatment temperature. The high-temperature complex cubic phase of Nitinol along with the effect of cold-working gives positive TCR and the onset of R phase with heat treatment reduces the TCR because in R phase the TCR is found to be negative. The continuous and large changes in TCR are due to the faster growth of R phase with heat-treatment temperature and the R phase is found to get stabilized above the heat-treatment temperature of 340°C .

The dependence of electrical resistivity in the heat-treated sample for the cooling part of the cycle is shown in figure 2b. A clear transition in TCR values is seen around 60°C as one comes from high temperature region to low temperature region. Further heating of the material above 210°C , the microstructure morphology of the alloy gets modified to

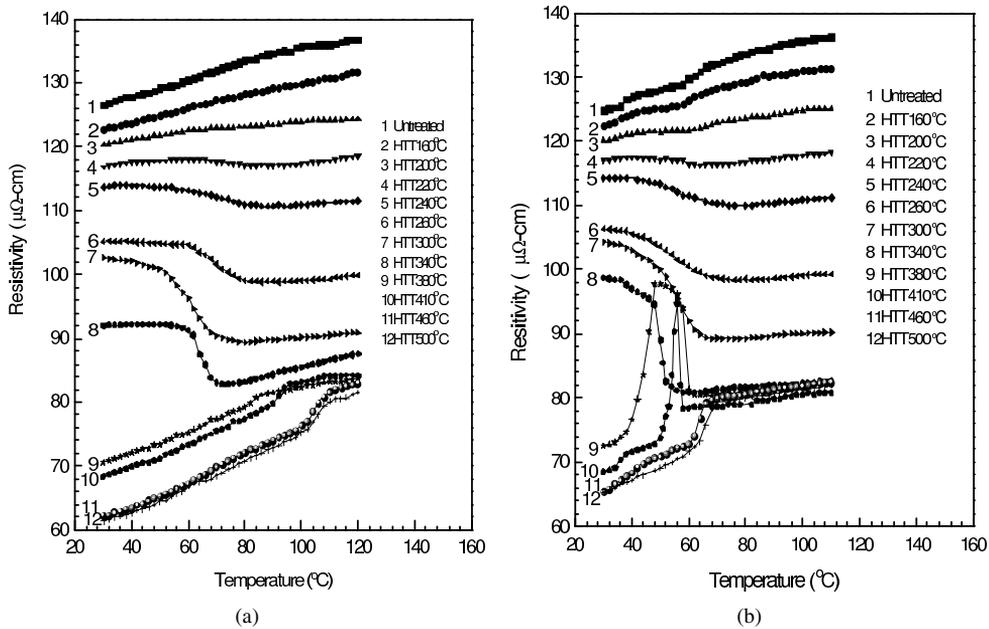


Figure 2. Temperature dependence of electrical resistivity of Nitinol heat-treated at different temperatures. (a) While heating and (b) while cooling.

accommodate R phase. It is observed that the R phase gets stabilized in the heat-treatment temperature range 340–410°C and electrical resistivity is found to have the maximum value of 98 $\mu\Omega$ cm for sample heat-treated at 340°C.

3.3 TMA characterization

Thermal expansion is one of the important engineering design parameters, particularly when it involves the solid-state phase transformations in a metal or in an alloy. Both DSC and ER techniques discussed above have certain limitations while determining the transformation temperatures in the presence of the mixed phases in SMA.

Figure 3a shows the thermal strain vs. temperature for the sample heat-treated at 400°C and 3b shows DSC thermogram of the same sample. At room temperature there exists a mixture of R and M phases. On heating, two types of transformations can be seen through endotherm splitting in DSC thermogram. The first peak corresponds to R→A transformation and the second peak is for M→A. But these two peaks are overlapped and hence it is difficult to determine the A_f^1 , which indicates the finish of R→A transformation. Thermal expansion plot shows a clear cap and determination of all transformation temperatures A_s^1 , A_f^1 , A_s and A_f is possible without ambiguity. The thermal expansion coefficient (TEC) is –ve for M↔A transformation and +ve for R↔A transformation. During martensitic transformation (A→M) the bcc crystal structure of parent austenitic phase transforms into a monoclinic crystal structure within a small temperature interval of 20°C. The lattice parameters given in the literature for the bcc phase is $a_0 = 3.015 \text{ \AA}$ and for the martensitic phase, $a = 2.889 \text{ \AA}$, $b = 4.120 \text{ \AA}$, $c = 4.622 \text{ \AA}$ [14]. When transformation takes place, there is a large increase in b and c combined with a small decrease in a . Therefore, the overall change in any direction is an increase in the cubic cell edge parameters and consequently a net increase in the dimension of the sample. Because of the expansion during a decrease in temperature, the –ve TEC results. On the other hand, during M→A transformation there is an overall decrease in all dimensions with an increase in temperature which results again in a –ve TEC. However, in A→R transformation, the bcc crystal structure transforms over to a rhombohedral crystal structure resulting in small changes in interaxial angles while suffering no change in unit cell edges [15]. Due to the distortion in the bcc phase during the formation process of the rhombohedral phase, a decrease occurs in the size in a given direction and hence, a contraction of the sample with a decrease in temperature is observed leading to a +ve TEC. Similarly, during R→A transformation the net effect is to result in an increase in cell parameter with increase in temperature leading to +ve TEC.

3.4 Space rotating platform

The aim has been to develop a fine rotating platform that can be used for space applications like, fine positioning of camera, deployment of flap or for conducting experiments in space stations or satellites etc. R↔A phase transformation in NiTi alloy is associated with a very small recoverable strain of the order of 0.5% compared to that of 6–8% recoverable strain in M↔A transformation. The stability of R↔A transformation against large number of thermal cycles is an attractive feature for an application of SMA. 40% cold worked NiTi

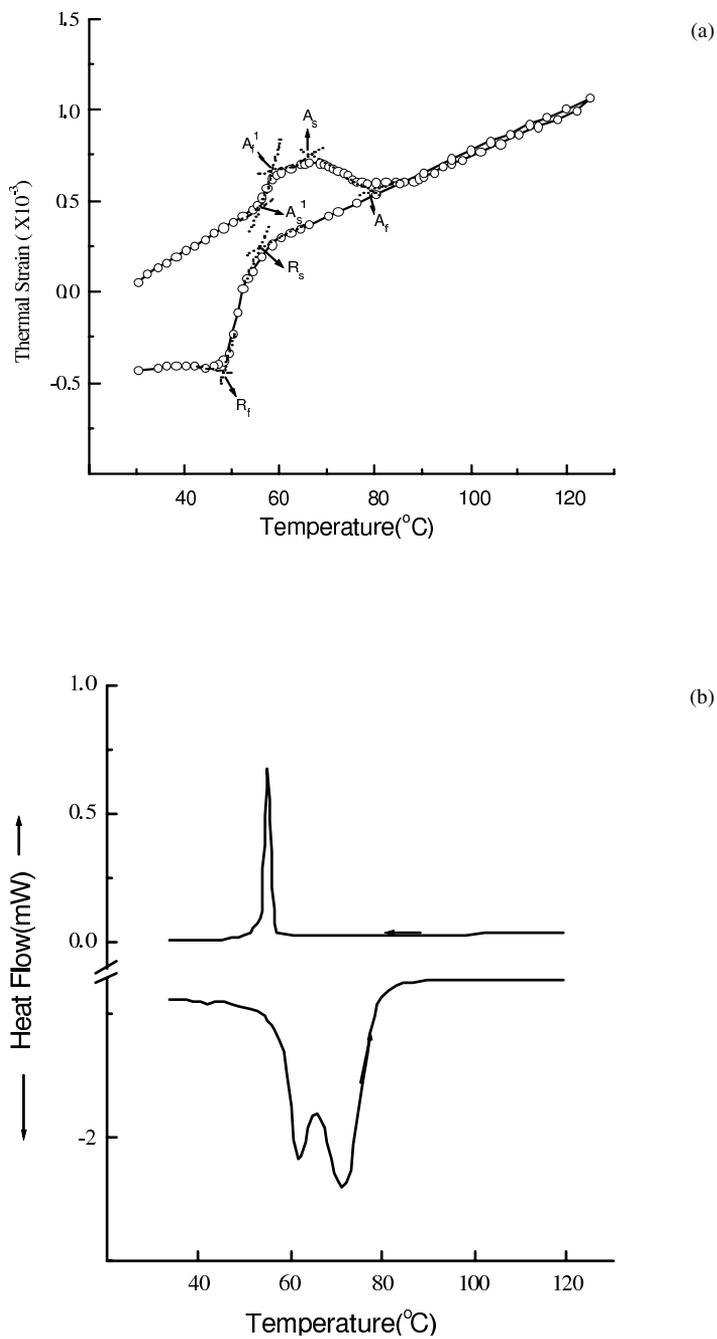


Figure 3. (a) Thermal strain vs. temperature for Nitinol heat-treated at 400°C. (b) DSC thermograms for Nitinol heat-treated at 400°C.

wire of 1 mm diameter has been characterized using the above techniques and the best conditions for the fabrication of an actuator have been obtained. A spring of NiTi has been designed and fabricated with appropriate heat-treatment such that martensitic transformation takes place through two-stage $A \rightarrow R \rightarrow M$. Further, the spring has been subjected to thermomechanical treatment for getting a two-way memory, viz., while heating the spring gets contracted and while cooling it gets elongated. This spring has been used as a thermal actuator and temperature change is confined between 50–65°C to utilize only $R \leftrightarrow A$ transformation. Linear stroke of 4 cm by the spring is used to rotate a platform carrying a load of 2 kg. The efficiency and reliability of the spring is tested over a million thermal cycles.

4. Conclusion

Near equiatomic prior cold worked (40%) Nitinol has been extensively characterized for its shape memory properties. In Nitinol wire when there exists a fully developed M phase at room temperature maximum recoverable strain can be obtained up to 9%. However, when there is a mixture of M and R, the strain is only up to 7%. Stable phases of A, R and M in 40% cold worked near equiatomic Nitinol is characterized by electrical resistivities which are found to be 82 $\mu\Omega$ cm, 98 $\mu\Omega$ cm and 65 $\mu\Omega$ cm, respectively. Thermal expansion probe using TMA is better suited to fix transformation temperatures whenever there is a mixed phase arising out of any heat treatment. Further, small recoverable strain of the $R \leftrightarrow A$ transformation can be effectively used for the applications of actuators over a large number of thermal cycles.

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