Dilatometric study of martensitic transformation in NiTiCu and NiTi shape memory alloys

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Dilatometric measurements have been carried out for the study of nature of martensitic transformation in the NiTiCu and NiTi shape memory alloy wire samples. Investigation has been done in the heat-treat temperature range 300–800°C. NiTiCu exhibits only single stage $A \rightarrow M$ martensitic transformation in the entire heat-treat temperature range indicating the suppression of R-phase by Cu substitution. NiTi shows the two-stage $A \rightarrow R \rightarrow M$ martensitic transformation in the heat-treat temperature range 340–410°C and the single-stage $A \rightarrow M$ martensitic transformation above heat-treat temperature 410°C. The extent of dilation during phase transformation decreases with increasing heat-treat temperature in both the alloys. Effect of first 15 thermal cycles on transformation temperatures in both the alloys has been studied. It is found that transformation temperatures are unaffected with thermal cycles in NiTiCu whereas considerable decrease in transformation temperatures has been observed in the case of NiTi. The stability of transformation temperatures in NiTiCu during $M \leftrightarrow A$ transformation against thermal cycling may be attributed to the associated smaller thermal hysteresis compared to NiTi. © *2001 Kluwer Academic Publishers*

1. Introduction
Shape memory alloys are typically functional materials. Their unique properties like thermal and mechanical memory and superelastic properties lend themselves to a variety of applications. The shape memory effect involves the reversible thermoelastic crystallographic phase transformation or martensitic transformation from a high temperature parent phase to a low temperature product phase [1, 2]. In general, there are two types of martensitic transformations viz., a single stage $A \rightarrow M$ and a two-stage $A \rightarrow R \rightarrow M$ where A is the high temperature austenitic phase, R is the intermediate rhombohedral phase and M is the low temperature martensitic phase. Authors have studied the two-stage martensitic transformation in NiTi using DSC and electrical resistivity measurements [3, 4]. The substitution of Cu for Ni in NiTi alloy affects the shape memory properties in many aspects. The existence of two-stage martensitic transformation in NiTiCu has been reported by many investigators through electrical resistivity (ER) and DSC measurements [5, 6]. Tae Nam *et al.* have shown that the substitution of Cu upto 10 at.% in NiTi exhibits the two-stage martensitic transformation and they have also shown the further addition of Cu will suppress rhombohedral phase and martensitic transformation results in a single stage $A \rightarrow M$ [7]. The uniaxial dilation with temperature is very sensitive to phase transformation in a material and can be used to study the transformation behaviours of a shape memory alloy. Quenching dilatometry has been used for the study of precipitation kinetics of Cu-Al-Ni shape memory alloys by Recarte *et al.* [8]. Authors have shown that dilatometric measurements are equally reliable in characterizing various phases of nitinol by comparing these with ER measurements [9].

The purpose of the present work is to investigate the nature of martensitic transformation in the NiTi and NiTiCu alloys using the dilatometric measurements. Temperature hysteresis is compared and the effect of early thermal cycles on transformation temperatures is discussed.

2. Experimental procedure
Commercially available near equiatomic 40% cold worked NiTi wire (50.03 at.% Ni and 49.97 at.% Ti) of diameter 0.8 mm used in this investigation is procured from Special Metals Corporation, USA and 20% cold worked NiTiCu wire (44.56 at.% Ni, 50.38 at.% Ti, 5.05 at.% Cu) of diameter of 0.8 mm has been made available by Memry Corporation, Belgium for this particular work. The dilatometric measurements are carried out using elongation probe of Thermomechanical Analyzer (TMA-50, Shimadzu). NiTiCu and NiTi wire samples, each of length of about 12 mm, are heat-treated at desired high temperature in the range 300–800°C in a muffle furnace. Each sample is annealed for 20 minutes at the pre-set high temperature and then quenched into water at room temperature. The sample is mounted

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between quartz probe connected to Linear Variable Differential Transformer (LVDT) and a quartz support tube. TMA is set for the elongation mode and a constant tensile load of 60 g is applied on the sample with the help of the force coil. Elongation is measured using LVDT, 0.1 μm being the accuracy of this measurement. The scanning temperature range is between 30°C and 120°C. Calibrated chromel-alumel thermocouple is used to measure the sample temperature. Heating and cooling rates are kept at 2°C/min. The measurements are recorded in a computer using an interface TA-50I.

3. Results and discussions

Uniaxial dilation is measured after offsetting the initial elongation brought about by the constant load of 60 g at room temperature. Fig. 1 shows a typical curve of

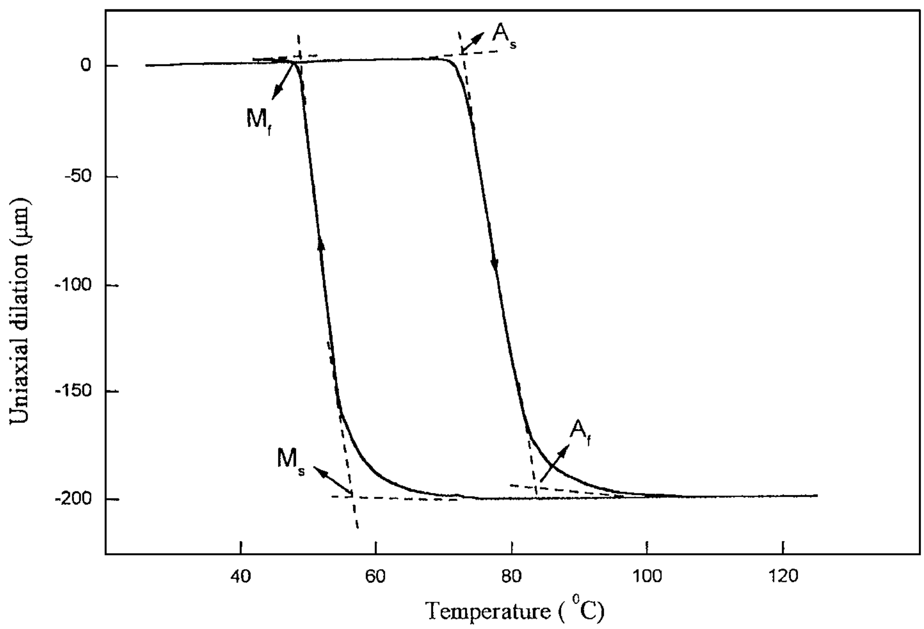

Figure 1 Typical uniaxial dilation Vs temperature curve of NiTiCu heat-treated at 500°C.

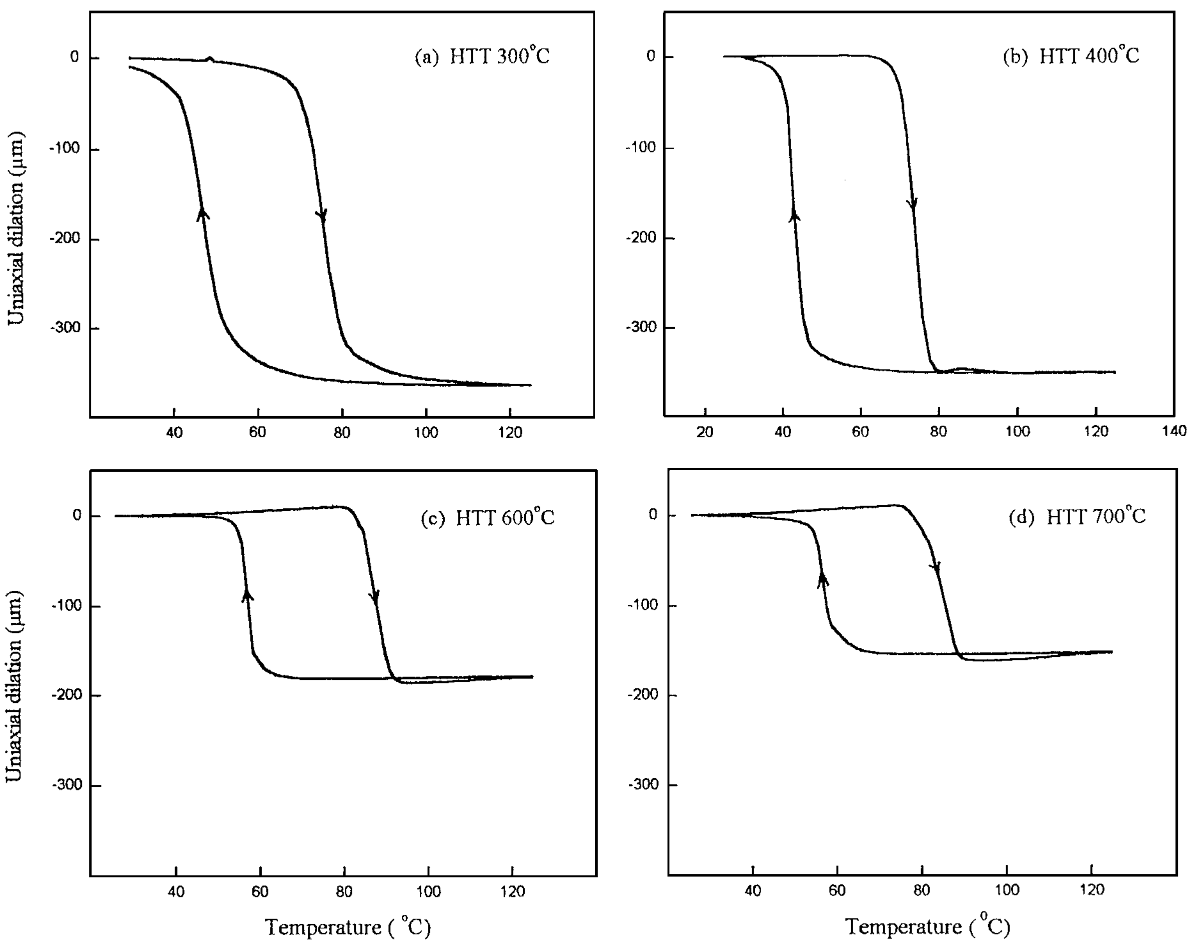

Figure 2 Uniaxial dilation as a function of temperature in NiTiCu at different heat-treat temperatures.

uniaxial dilation as a function of temperature for the NiTiCu sample heat-treated at 500°C. Abrupt and large changes in uniaxial dimension are observed during heating and cooling at certain temperatures. These are attributed to phase transformations taking place in the material [10]. M → A transformation during heating causes sudden contraction whereas the sudden expansion during cooling is due to A → M transformation. On heating, a normal expansion is observed till about 72°C and then it starts contracting. The contraction of the sample continues till it reaches 84°C and again there appears normal expansion above this temperature. While cooling, the sample starts expanding at around 58°C after usual contraction. This expansion continues till about 48°C and thereafter, the expected contraction takes place with decreasing temperature. To fix the transformation temperature tangents are drawn at the points where there are changes in the slope of dilation curve. The point of intersection of tangents is taken as the appropriate transformation temperature. The temperature at which the contraction begins while heating is A_s and the temperature at which contraction terminates is A_f. Similarly, on cooling the onset of the expansion is at M_s and the temperature at which expansion gets terminated is M_f.

Fig. 2a–d give the temperature dependence of uniaxial dilation of the NiTiCu wires heat-treated at 300°C, 400°C, 600°C, & 700°C, respectively. The

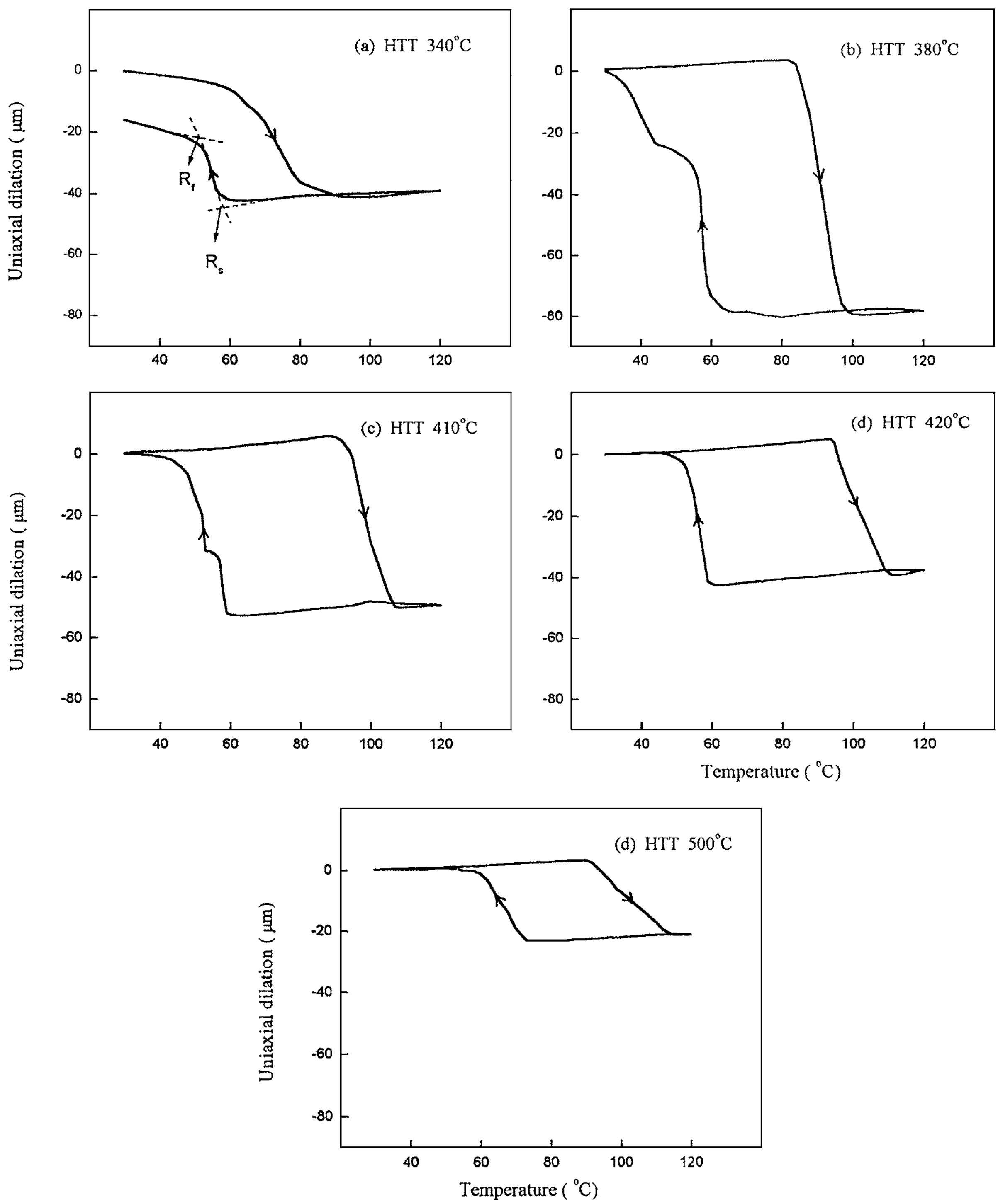

Figure 3 Uniaxial dilation as a function of temperature in NiTi at different heat-treat temperatures.

TABLE I Comparison of transformation temperatures in NiTiCu and NiTi alloys at different heat-treat temperatures

HTT (°C)	Samples	A_s (°C)	A_f (°C)	R_s (°C)	R_f (°C)	M_s (°C)	M_f (°C)
400	NiTiCu	68	80	—	—	50	38.8
	NiTi	91.9	104.3	59.9	56.9	51.8	37.7
500	NiTiCu	72.4	84.4	—	—	57.8	48.5
	NiTi	96.9	114.4	—	—	71.0	59.1
600	NiTiCu	81.5	93.1	—	—	62.1	51.5
	NiTi	98.1	118.0	—	—	74.3	62.9
700	NiTiCu	78.4	90.6	—	—	62	51.8
	NiTi	96.1	117	—	—	74	62.8

transformation temperatures A_s, A_f, M_s and M_f are found to increase with increasing heat-treat temperature. Fig. 3a–e show the dilation curves of the NiTi wire heat treated at 340°C, 380°C, 410°C, 420°C and 500°C respectively. Heating part of the dilation curves are similar to that observed in the NiTiCu samples. In the case of the samples heat-treated at 340°C, 380°C and 410°C a small step is observed during cooling. This step is attributed for the appearance of the R-phase and martensitic transformation takes place in two stage, $A \rightarrow R \rightarrow M$. On cooling, the sample normally contracts till R_s and then suffers sudden expansion as seen in Fig. 3a. This large expansion partially gets terminated at R_f and there is a relatively small expansion on further cooling the sample. Again large expansion starts at M_s and with decreasing temperature expansion decreases. This feature is not visible in Fig. 3a because M_s is much below the room temperature for the corresponding heat-treat temperature. When the Nitinol sample is heat-treated just above 410°C the step in the cooling part of the cycle gets disappeared indicating the absence of R-phase (Fig. 3d). Therefore, 410°C is considered to be the upper critical heat-treat temperature (HTT) of the sample to sustain R-phase. It is observed from Fig. 3a–e that increase in heat-treat temperature shifts transformation temperatures A_s, A_f, M_s and M_f towards the higher temperature region whereas R_s remains fairly constant and R_f gets shifted very slightly towards the higher temperature. However beyond heat-treat temperature 680°C one observes these transformation temperatures start decreasing slightly. Table I gives the transformation temperatures of NiTiCu and NiTi at various heat-treat temperatures.

The effect of early thermal cycles is studied in both the alloys. Fig. 4a and b give the dilation curves after each thermal cycling of NiTiCu and NiTi alloy heat treated at 500°C, respectively. Observations are done upto 15 thermal cycles. In the case of NiTi the effect of thermal cycling is to decrease the transformation temperatures considerably as seen in Fig. 4b. A_s and A_f are decreased at about 12°C on 15 thermal cycles and M_s and M_f get decreased by about 10°C. In the case of NiTiCu, transformation temperatures are found to be unafected by thermal cycling and the dilation curves remain overlapped as seen in the Fig. 4a. In this case the changes in the dilation during $M \leftrightarrow A$ transformation also remain fairly constant upto 15 thermal cycles.

The change in the dilation during $M \rightarrow A$ transformation is negative whereas the change in dilation during

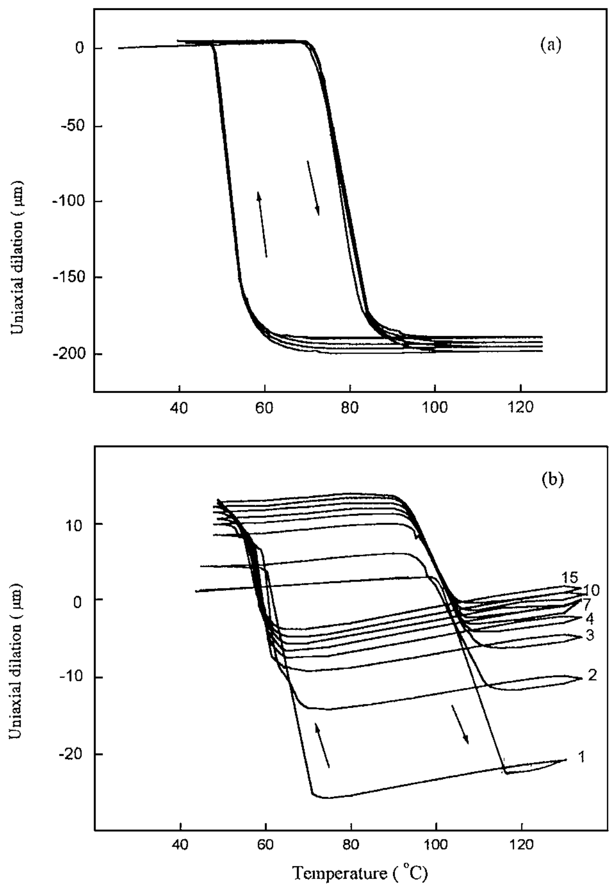

Figure 4 Effect of first 15 thermal cycles on $M \leftrightarrow A$ transformation in (a) NiTiCu wire heat-treated at 500°C; (b) NiTi wire heat-treated at 500°C.

$A \rightarrow M$ transformation is positive both in NiTiCu and NiTi wires. Another significant point of observation is that the change in uniaxial dilation brought about by $M \rightarrow A$ transformation continuously decreases with increasing heat-treat temperature in the case of both the alloys. When the material is annealed at higher heat-treat temperature grain size increases and in turn it decreases the internal stress [11]. This can be observed from the continuous decrease in the extent of dilation during phase transformations as seen in Fig. 2a–d and Fig. 3a–e. The larger contraction resulting in the samples heat-treated at lower temperatures during $M \rightarrow A$ transformation is due to the addition of the internal thermal stress to the prevailing tensile stress corresponding to the applied load of 60 g. With increase in heat-treat temperature, the internal thermal stress decreases due to increase in the grain size and as a result the observed contraction decreases.

From literature it is found that Ti_3Ni_4 precipitation in a NiTi based alloys plays an important role in the formation of R-phase [12, 13]. The addition of Cu is effective in preventing this precipitation [14]. Hence in the case of NiTiCu alloy the rhombohedral phase is suppressed and only a single stage martensitic phase $A \rightarrow M$ is observed in the entire heat-treat temperature range 300–800°C. But in the case of NiTi alloy two-stage martensitic transformation is observed in heat-treat temperature range 340–410°C. The thermal hysteresis associated with $M \leftrightarrow A$ transformation in NiTiCu is smaller when compared with that of the NiTi alloy.

In general, whenever the thermal hysteresis is small, the effect of thermal cycling is less. The authors have observed the thermal hysteresis of ∼40°C in M ↔ A and ∼10°C in R ↔ A transformation and it was shown R ↔ A is hardly affected by thermal cycling [3]. The present dilatometric studies also give thermal hysteresis of 46°C for M ↔ A transformation in NiTi whereas it is 26°C for M ↔ A transformation in NiTiCu. Hence, in the case of NiTiCu alloy the stability of transformation temperatures against thermal cycling can be taken to be associated with smaller thermal hysteresis.

4. Conclusions

1. NiTi shows the two-stage martensitic transformation in the heat-treat temperature range 340–410°C and the single-stage martensitic transformation for heat-treat temperature above 410°C whereas NiTiCu show only the single-stage martensitic transformation throughout the heat-treat temperature range 300–800°C.

2. The change in dilation during M → A transformation is negative and A → M and A → R is positive in both NiTi and NiTiCu.

3. The change in dilation during phase transformation goes on decreasing with increasing heat-treat temperature in both the alloys.

4. Early thermal cycles have no effect on the transformation temperatures of NiTiCu whereas there is considerable decrease in transformation temperature of NiTi with early thermal cycles.

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