Journal of Thermal Analysis and Calorimetry, Vol. 70 (2002) 199–207

DMTA STUDY OF A NICKEL-TITANIUM WIRE

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Abstract

The nickel–titanium alloys are usually known as Shape Memory alloys because of their ability to return to some previously defined shape or size when subjected to the appropriate thermal procedure. Mechanical properties of a nickel titanium wire were investigated by DMTA using cylindrical tension mode. The Young's modulus, the maximum strain and residual deformation have been calculated. Recovery of previously deformed samples was observed in constant stress temperature ramp tests. Relaxation stress behaviour at temperatures above the austenitic transformation has been studied. The strain and frequency ranges of linear response have been determined by dynamic experiments. Strain amplitude of 0.1% and frequency of 1 Hz have been chosen for the temperature ramp dynamic experiments. A big change between 65 and 95°C is observed in the storage modulus. The values of E' at temperatures below and above the transition are essentially constant. Finally, the effects of the frequency at different temperatures have been examined.

Keywords: DMTA, elastic moduli, nickel–titanium alloys

Introduction

The shape memory effect in near equal-atomic Ni–Ti alloys was first found by Buehler *et al*. in 1963 [1]. These alloys show a phase transformation when cooled from austenite (high temperature phase or parent phase) to martensite which has a good formability. Thus, they can be deformed easily at low temperatures. If alloy is heated up to transformation temperatures, austenite appears again and the previous shape is recovered. The interval of temperature of the transformation of nitinol alloys is between –200 and 100°C and the shape recovery process occurs over a range of just a few degrees.

The austenitic phase (β) has a CsCl order structure with a_0=3.015 Å and the most common martensitic structure (B19′) is monoclinic with a=2.889, b=4.120, c=4.622 Å and β=96.8° [2]. This transformation does not happen in a single step but

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in two since it has been confirmed the existence of an intermediate phase called R-phase with rombohedral structure. TiNi phase has a very narrow interval of composition at temperatures below 630°C (from 50.0 to 50.5 atom% of Ni). If nitinols with more than 50.5 atom% are quenching from temperatures above 630°C, TiNi phase is retained at room temperature. TiNi is an unstable phase at low temperature and it can be transformed on aging in other phases according to the following sequence [3]

$$TiNi\rightarrow Ti_3Ni_4\rightarrow Ti_2Ni_3\rightarrow TiNi_3$$

These precipitation reactions can be monitored by mechanical properties measurements. Ti_3Ni_4 and Ti_2Ni_3 phases do not occur if aging is above 750 and 800°C respectively.

When a physical property (length specimen change, volume specimen change, heat flow, electrical resistance, etc.,) of the material related to transformation of the phase is plotted *vs*. temperature, Ni–Ti alloys show hysteresis. Hysteresis of shape memory alloys is characterized by four important temperatures: martensite initial temperature (M_s), martensite final temperature (M_f), reverse transformation initial temperature (A_s) and reverse transformation final temperature (A_f).

Factors like nickel content, aging, cold work, thermomechanical treatment and addition of alloying elements have an influence over shape memory behaviour [4, 5]. Slight change in the Ni–Ti composition can originate a large difference in the properties of the NiTi alloy, particularly in its transformation temperatures. Thus it is preferable to characterize more accurately these alloys by its martensiteaustenite final temperature (A_f). Two of these factors are the heating rate and the application of cycling stresses to Ni–Ti alloys. DSC is one of the classic techniques to determinate transformation temperatures. On heating, DSC curves show an endothermic peak in which A_s and A_f are the beginning and final temperatures of the peak, whereas on cooling there is an exothermic peak in which M_s and M_f can be calculated. Another thermal analysis techniques as TMA and DMA have been used to understand the influence of applied stress on transformation temperatures [6, 7]. DMTA, dynamical mechanical thermal analysis, offers the possibility of studying temperature transformation and applying cycling stress at the same time.

Experimental

All the samples were taken from a 0.05 mm diameter wire of Flexinol 050, manufactured by Mondo-tronics, Inc. It is specified as a equal-atomic Ni–Ti alloy. Induced couple plasma experiments (ICP) confirmed that composition.

All the tests were performed in a Rheometric Scientific's DMTA IV operated under cylindrical tension mode.

Steady and dynamic experiments were conducted. The steady experiments were strain rate test, constant stress temperature ramp and stress relaxation test. The dynamic experiments, on different conditions, gave the evolution of the tensile storage modulus, tensile loss modulus and loss tangent.

A phase change involves variations in tensile storage modulus ($E'=\sigma_{t0}\cos\delta\varepsilon_0$), tensile loss modulus ($E''=\sigma_{t0}\sin\delta/\varepsilon_0$) and loss tangent ($\tan\delta=E''/E'$); where σ_{t0} is the maximum applied stress, ε_0 is the maximum resulting stress, δ is the phase lag and tan is the loss tangent.

Results

Strain rate tests have been performed at rates of $5.00\cdot10^{-5}$ and $1.00\cdot10^{-4}$ s^{-1}. In some cases the direction of the test has been reversed from tension to compression in order to check the hysteresis behaviour. Figure 1 shows a typical curve of one experiment at $1.00\cdot10^{-4}$ s^{-1}.

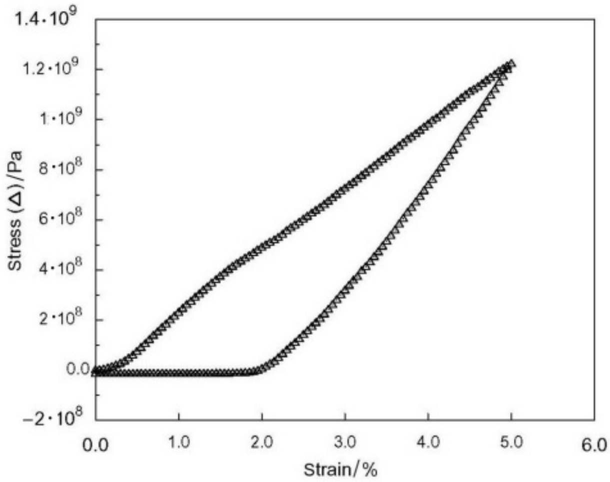

Fig. 1 Trace of a strain rate test at $1.00\cdot10^{-4}$ s^{-1}

In other experiments the tension strain rate has been kept upon breaking the sample, as it is shown in Fig. 2.

Constant stress temperature ramps have been applied to the samples after the hysteresis experiment previously described. Stresses of $8.0\cdot10^6$ Pa, in some cases, and $2.3\cdot10^8$ Pa, in others, have been kept while applying a ramp from 25 to 120°C at a rate of 5 K min^{-1}. The ramp was followed by an isothermal segment of 300 s at 120°C and, finally, the sample was cooled down to 25°C at 5 K min^{-1}. Figure 3 plots the overlay of two experiments where different constant stresses have been applied.

A special stress relaxation test has been performed. It consisted in applying a step strain of 5% and heating quickly up to 110°C. This temperature was reached in about 130 s and was kept constant for 370 s more. Figure 4 shows the curves of strain, stress and temperature *vs*. time.

Plots of dynamic strain sweep and dynamic frequency sweep experiments are shown in Figs 5 and 6, respectively. They have been used for choosing the conditions for dynamic experiments where temperature was ramped. Figure 7 shows how the storage modulus changes while heating and cooling at 5 K min^{-1} from a sample that has been previously subjected to a hysteresis experiment.

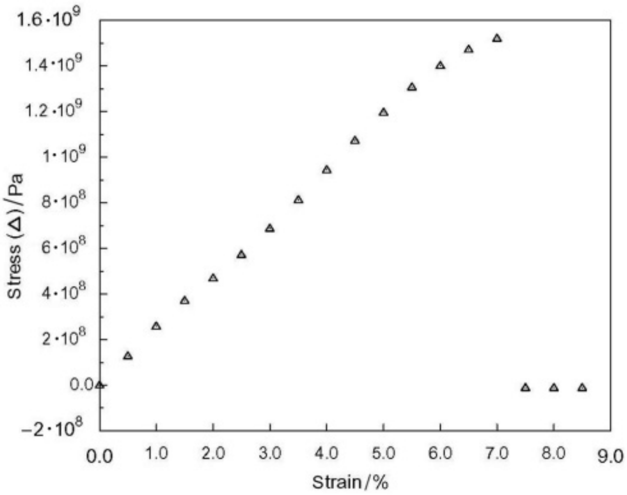

Fig. 2 A tension strain rate at $5\cdot10^{-5}$ showing the breaking of the sample at a strain between 7.0 and 7.5%

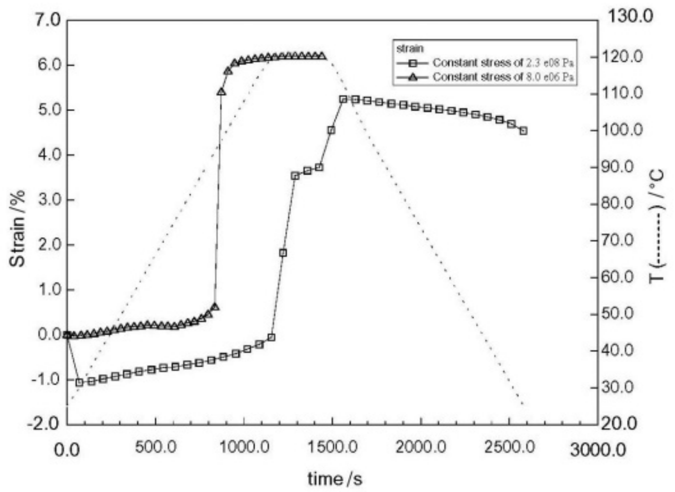

Fig. 3 Overlay of two constant stress temperature ramps where different stresses have been applied. The samples were previously subjected to hysteresis experiments

Figure 8 plots the results from a frequency/temperature sweep test where a scan of frequencies has been performed at each of the 9 steps of temperature between 30 and 110°C. The strain amplitude was 0.1%.

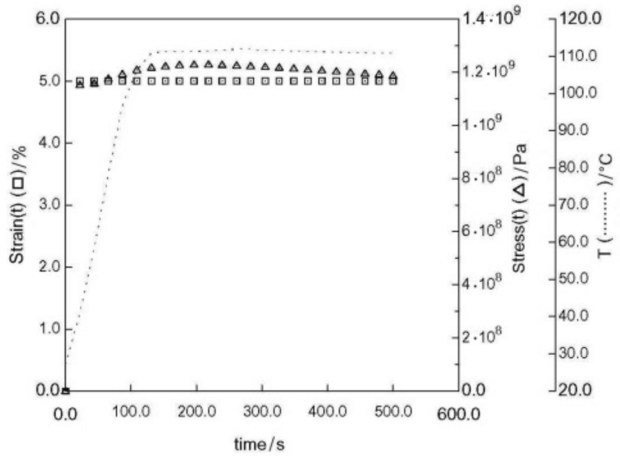

Fig. 4 Traces of strain, stress and temperature *vs*. the time in a relaxation test of Flexinol 050 L

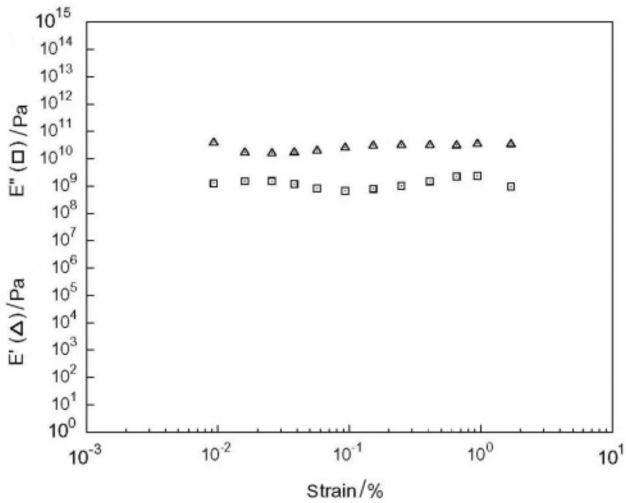

Fig. 5 Storage and loss modulus in a dynamic strain sweep where the frequency was 1 Hz

Discussion

The modulus, calculated from the linear region of the strain rate tests is 262.3 MPa. The break happens at about 7% strain, as it is shown in Fig. 2. Other authors described a double of this strain at tempertures above 100°C [8, 9]. The samples subjected to the hysteresis tests, where a strain of 5% was reached, kept at the end of the

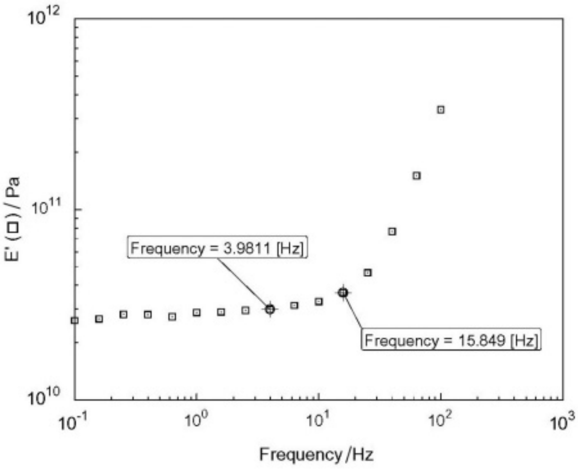

Fig. 6 Storage modulus in a dynamic frequency sweep where the strain amplitude was 0.01%

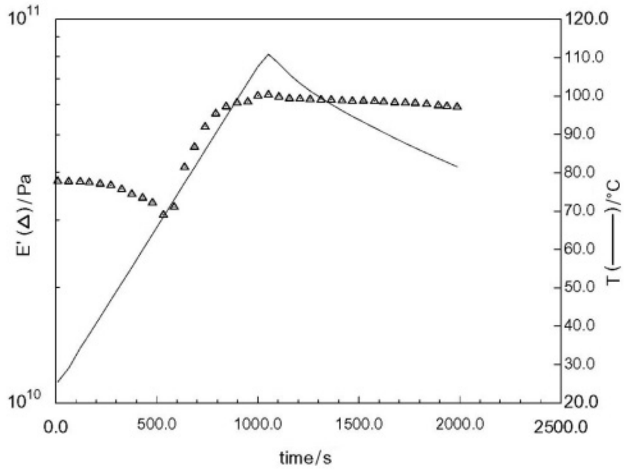

Fig. 7 Evolution of the storage modulus with the time where the temperature was ramped as it appears on the plot. Obtained from a sample previously subjected to a hysteresis experiment

test a plastic deformation of about a 2%. Other authors found a permanent deformation of about 3% after a strain of 4% in a Ti–50.2 atomic% Ni alloy [10].

Figure 3 shows how these samples shorten when the temperature increases allowing the phase transition. The effect of the constant stress applied during the experiment is noticeable. When applying a stress of 8.0 MPa an abrupt change starts at 87.99°C, while when applying 2300 MPa that change does not start until 109.66°C. Maximum recovery is in the both cases higher than the plastic deformation obtained by the hysteresis experiment. It is also clear that the higher the applied constant stress the lower the maximum recovery. In this experiment, the curve obtained at higher constant stress exhibit a delay in the transition of about 260 s.

Figure 4 was obtained from a stress relaxation test consisting in to apply a step strain of 5% and quickly heating upon reaching 110°C, which has been held for 270 s. A very slow relaxation of stresses is observed at that temperature, over the transition temperature.

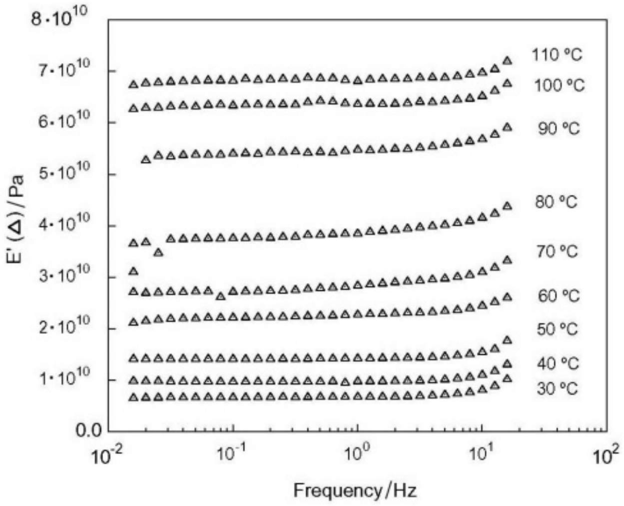

Fig. 8 Plots of the storage modulus obtained from 9 scans of frequency at equally spaced steps of temperature between 30 and 110°C, where the strain amplitude was 0.1%

The use of dynamic experiments was considered in order to calculate the storage modulus (E') and loss modulus (E''). For setting up the conditions for the dynamic experiments, two kinds of experiments have been performed: dynamic strain sweep and dynamic frequency sweep.

A frequency of one Hz has been used for the dynamic strain sweep. Figure 5 shows that there is not important variation of E' and E'' in the range from 0.01 to 1% of strain.

Figure 6 shows that the effect of the frequency on E' is not important in the range from 0.01 to 3.98 Hz. At values above 15.85 Hz the effect of the frequency on E' is dramatic.

The traces shown in Fig. 7 were obtained from a sample previously subjected to a hysteresis experiment. The same behaviour was observed in fresh samples. There is in general a constant value of E'' at temperatures below the phase transition and a higher value of E' at temperatures above the transition. But once the transition happen, the value of E' is kept constant as the temperature decreases. Other important fact is that a drop in the E' values precedes the quick growth due to the phase transition. It could be due to relaxation effect of the temperature in the martensite phase.

An important increase of the storage modulus is observed between 65 and 95°C, this behaviour was attribuided by other authors [11, 12] to the martensite-austenite transformation.

Finally, Fig. 8 plots the storage modulus vs frequency at different temperatures. It is noticeable that the distance between the traces increases at temperatures around 80 to 90°C. All the curves exhibit a linear dependence of E' with the frequency in the range from 0.01 to 2 Hz. Table 1 shows that the slope of the linear part of the curves increases at temperatures around the transition temperature, with maximum slope at 80°C. This mean a higher dependence of E' with the frequency at temperatures close to the transition temperature.

Table 1 Slopes in the linear region (from 0.015 to 2 Hz) of the storage modulus curves showed in Fig. 8

T/°C	30	40	50	60	70	80	90	100	110
Slope·10^8	1.1	–0.25	0.75	6.6	9.0	13	7.6	4.6	4.0

Conclusions

A near equal-atomic nickel titanium alloy was studied by DMTA in stationary and dynamic modes.

The Young's modulus at 25°C was 262.3 MPa, and the maximum strain about 7%.

A remaining plastic deformation of 2% was observed after applying a 5% strain.

The observed recovery in constant stress temperature ramp tests resulted to be higher than the plastic deformation previously imposed to the samples. The recovery is shifted to higher temperatures as higher constant stress is applied.

Slow relaxation of stresses was observed at temperatures above the austenitic transformation.

An important increase of the storage modulus is observed between 65 and 95°C.

At temperatures enough below and above the transition, the modulus is almost constant in a broad range of frequencies while, at temperatures close to the transition, a strong effect of the frequency is observed in the storage modulus.

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The authors gratefully acknowledge FEDER (1FD97-1262) and XUGA (PGIDT–PXI16602A) for providing support to undertake this project.

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