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Section 7. Metallurgy

Determination of some mechanical properties of TiNi (50.6 at. % Ni*)* shape memory alloy using dynamic mechanical analysis and tensile tests

D. BATALU, H. GUOQIU[a], A. ALOMAN, L. XIAOSHAN[a], Z. ZHIHUA[b]
Materials Science and Physical Metallurgy Department, "Politehnica" University of Bucharest, Romania
[a]School of Material Science and Engineering, Tongji University, China
[b]Pohl Institute of Solid State Physics, Tongji University, China

There were studied some mechanical properties of TiNi (50.6 at. % Ni) shape memory alloy, using dynamic mechanical analysis and tensile tests. The aim of our studies was to point out a correlation between the mechanical behaviour and the martensitic transformation of the alloy during heating/cooling process. A difference between stabilization of the mechanical properties and the martensitic transformation was observed. The heat treatment parameters necessary for inducing the shape memory effect or the superelasticity of the alloy are, also, presented in this paper.

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1. Introduction

TiNi shape memory alloys are one of the most interesting materials, due to their shape memory effect and the superelasticity property. Based on these properties, TiNi shape memory alloys have a large range of applications as smart materials. Because TiNi shape memory alloys have a good biocompatibility they are suitable for producing medical devices and implants [1,2]. Our research concerns the characterization of TiNi (50.6 at. % Ni) shape memory alloy, used for producing self-expandable and balloon-expandable stents.

The aim of our studies is to point out a correlation between the mechanical properties and the martensitic transformation of the alloy during heating/cooling process. TiNi (50.6 at. % Ni) shape memory alloy was chosen for the convenient way of controlling the phase transformation temperatures through thermo-mechanical treatments [3,4]. TiNi shape memory alloys have a fair good plasticity in the martensitic state and an improved elasticity in the austenitic state.

2. Materials and methods

Through dynamic mechanical analysis (DMA) and tensile tests we established the heat treatment parameters for inducing shape memory effect and superelasticity in TiNi (50.6 at. % Ni) alloy. For DMA, heat treated and as cold rolled samples were used. Differential scanning calorimetry (DSC) was also used for establishing the martensite ↔ austenite phase transformation temperatures. The tensile tests were realized on a testing machine, equipped with a furnace for controlling the testing temperature.

The results of study show that TiNi (50.6 at. % Ni) shape memory alloy is suitable for producing both self-expandable stents, and superelastic stents. In the case of self-expandable stents a high recovery rate can be achieved, but it can be considered the summation of superelasticity and shape memory effect. A difference between the stabilization temperatures of the mechanical properties and the martensite ↔ austenite phase transformation temperatures was observed.

TiNi (50.6 at. % Ni) shape memory alloy, produced at METAL PRODUCTS Research Institute of Shanghai, China, was used for the research. The final products were obtained by cold drawing, with a final grade of deformation of 15 %.

The tests of dynamic mechanical analysis (DMA) were performed with a DMA Universal V 2.4 F – TA analyzer. Sheet samples of 0.18 mm thickness, 4 mm width and 16.5 length were used for tests. The temperature range of tests was from – 50 ºC to +100 ºC, the heating rate was 5 ºC/ minute, and the operating frequency was 1 Hz. The tests were performed on the as cold rolled samples, without heat treatment, and on samples that were heat treated for inducing shape memory effect. The heat treatment for inducing the shape memory effect was carried out in two steps: 1. the sample was first solution heat treated at 800˚C, for 20 minutes, and then quenched in water-ice mixture; 2. after quenching, the sample was aged at 400 ˚C for 90 minutes, followed by furnace cooling.

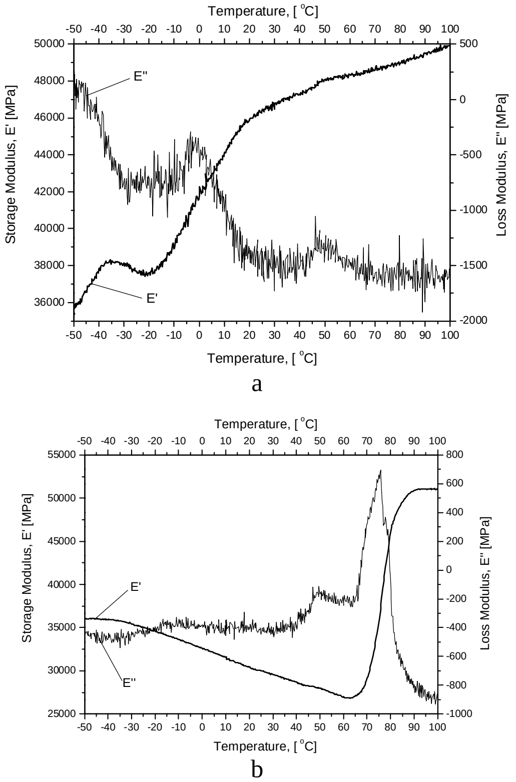
The tensile tests were performed on a testing machine equipped with a furnace for controlling the temperature. The samples used for tests were wires of 0.8 mm diameter, and 120 mm length. The results of two types of heat treatment were analyzed. The first type of heat treatment (HT1) was applied for inducing the two-way shape memory effect. The sample was first solution heat treated at 700 ˚C, for 20 minutes, and then quenched in water-ice mixture. After quenching the sample was aged at 400 ˚C for 60 minutes, and then quenched in water-ice mixture. The second type of heat treatment (HT2) was the annealing of different samples at

350, 450 and 550 °C, for 30 minutes, followed by water quenching.

A Perkin-Elmer DSC-4 differential scanning calorimeter was used for establishing the martensite ↔ austenite phase transformation temperatures. The heating rate was 2 °C/ minute.

3. Results

Both DMA tests performed on the as cold rolled samples (without heat treatment), and on samples that were heat treated for inducing shape memory effect show a variation of loss modulus (E") and storage modulus (E') versus temperature (Fig. 1 a, b). In the martensitic state the storage modulus has a low value and it is incresing gradually with the temperature, forming a plateau at high temperature (more evident for the heat treated sample, Fig. 1 b).



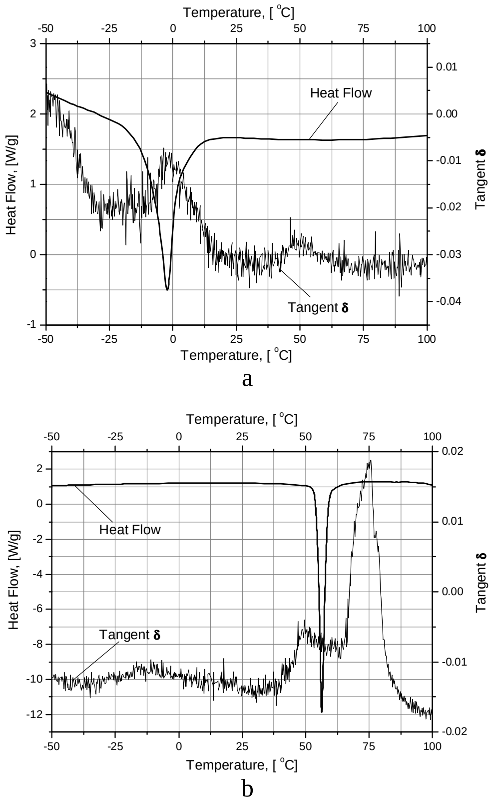
a

b

Fig. 1. Variation of storage and loss modulus versus temperature for: a. the as cold rolled sample (without heat treatment), b. the heat treated sample.

Variation of storage modulus versus temperature is more rapid for the heat treated sample than for the as cold rolled sample. A stabilization plateau appears at high temperature (over 90 °C) for the heat treated sample (Fig. 1b).

The tangent of phase difference (tangent δ) provides information on the relationship between the elastic and inelastic component, and it is given by the ratio E"/E'. The highest peak of tangent δ coincides with martensite ↔ austenite phase transformation for the as cold rolled sample, but it is quite far from the peak determined by DSC method in the case of the heat treated sample (Fig. 2 a, b).



a

b

Fig. 2. *Variation of heat flow and tangent δ versus temperature for:* ***a.*** *the as cold rolled sample (without heat treatment),* ***b.*** *the heat treated sample.*

Through DSC tests (performed during heating, from -50 °C to 100 °C), and DMA tests as well, was pointed out the phase transformation. In the as cold rolled sample can be also observed the martensite ↔ austenite phase transformation; in this case, the martensitic phase was induced by cold work. The transformation temperatures are much lower than those of heat treated samples (Fig. 3).

The as cold rolled samples (without heat treatment) show a poor elasticity, the recovery rate being just 3 % on the strain scale (Fig. 4).

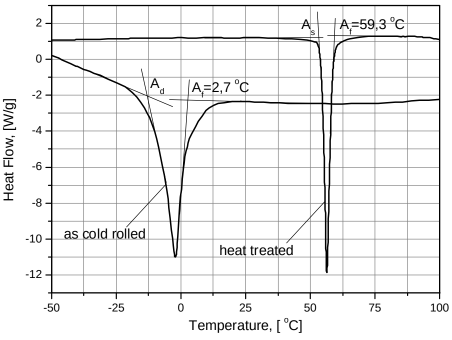


Fig. 3. Variation of heat flow versus temperature for the as cold rolled and the heat treated samples.

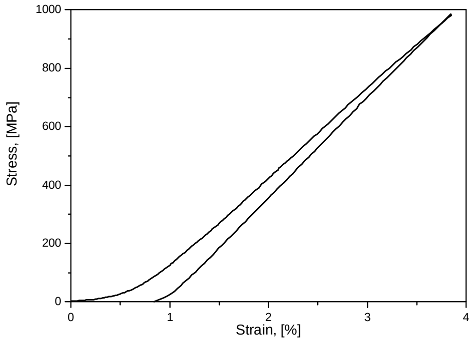
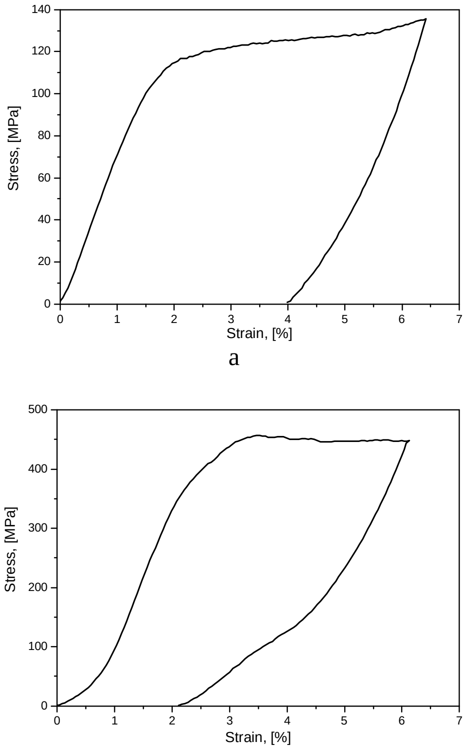


Fig. 4. Stress-strain curves for the as cold rolled sample. Recovery rate at room temperature, 3 %.

After the first type of heat treatment (HT1) was applied for inducing the two-way shape memory effect, a poor recovery rate was observed at room temperature, but it increased with more than 1 % at 60 ^{o}C (Fig. 5. a, b). The increasing of recovery rate with the temperature is due to the contribution of the shape memory effect.

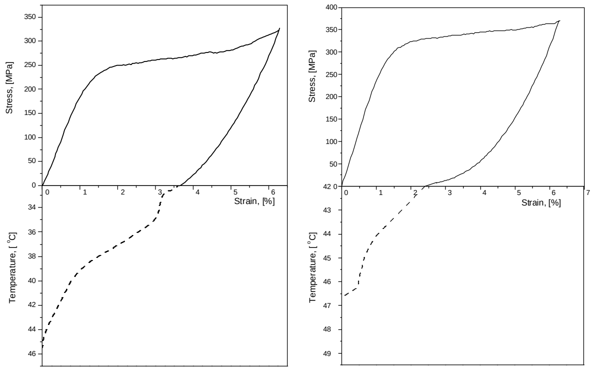


a

b

Fig. 5. Stress-strain curves for the annealed samples at 350 ºC. a. Recovery rate at room temperature, 2.39 %. b. Recovery rate at 60 ºC, 4 %.

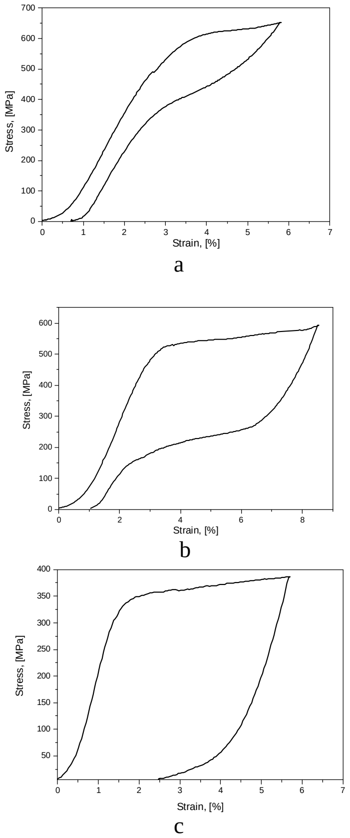
The recovery rate of the heat treated samples (in order to induce the two-way shape memory effect, HT1), can be explained as the result of superposition of elasticity and shape memory effect of the alloy. If at room temperature the recovery rate of the alloy is 2.6 % (Fig. 6.a, b - the upper side), increasing the temperature, the alloy will continue to recover its shape due to the shape memory effect (Fig. 6.a, b – lower side).



a b

Fig. 6. Stress-strain curves (upper side), and the result of shape memory effect (lower side). a. Recovery rate at room temperature, 2.6 %. b. Recovery rate at 42 ºC, 4 %.

The annealing heat treatment (HT2), does not induce the shape memory effect, but improves effectively the superelasticity. The variation mode of recovery rate versus annealing temperature indicates a maximum of superelasticity (Fig. 7. a, b, c).



a

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c

Fig. 7. Stress-strain curves for the annealed samples at: a.. 350 °C, recovery rate, 5.25 %. b. 450 °C, recovery rate,7.5 %. c. 550 °C, recovery rate, 3.25 %..

4. Discussion

The tests were useful in pointing out the mechanical behavior of TiNi (50.6 at. % Ni) shape memory alloy, in different states (cold rolled, heat treated – HT1, annealed – HT2).

As a result of dynamic mechanical analysis, the variation of storage and loss modulus versus temperature can be observed. It can be observed a more rapid and clear variation of the storage and loss modulus for the heat treated sample (HT1, Fig. 1b), than for the as cold rolled sample (Fig. 1a). We suppose that for the cold rolled sample, without heat treatment, a partial phase transformation occurred. At low temperature, the alloy was not fully in the martensitic state. The martensite phase was induced by cold work, and the austenitic phase was partially transformed into martensitic phase. X-ray diffraction and microstructure studies are necessary in order to elucidate this assumption.

It can also be noted the plateau formed after the phase transformation ended, in the case of the heat treated samples. This indicates a stabilization of mechanical properties, compared with the as cold rolled sample, where the storage and loss modulus vary continuously with the temperature.

The DMA show a prominent peak, corresponding to the martensite ↔ austenite phase transformation, and other smaller peaks can be observed as well. They may indicate the existence of the R-phase, but the DSC determination does not point them out. Hence, DMA can be considered a complementary test, beside DSC tests, usually used for determination of martensite ↔ austenite phase transformation temperatures.

A difference between stabilization of the mechanical properties and the martensitic transformation was observed for the heat treated sample (Fig. 2b). DSC results show that the phase transformation is completed at about 59.3 ^{o}C (A_f - austenite transformation finish temperature; A_s - austenite transformation start temperature; A_d - austenite transformation start temperature induced by cold work), but according with the DMA results, the mechanical properties start to stabilize at around 90 ^{o}C. This observation could be very important for practical applications.

Even though it is possible to induce a martensite ↔ austenite phase transformation through cold working, the heat treatments can be considered the finest instrument for controlling the phase transformation temperatures and other properties.

The tensile tests are a simple method for determination some mechanical properties and the recovery rate. The cold work introduces internal residual stress and a high density of lattice defects that will affect the mobility of the martensite interfaces. At high temperatures of heat treatment, the internal stress and lattice defects are decreasing, influencing the mechanical properties (Fig. 4 - 7).

Some heat treatments (HT1) can generate precipitation processes, reducing the mobility of martensite interfaces. For the as cold rolled samples (without heat treatment, Fig. 4), the elasticity is quite low (3 %). At higher stress degree, at room temperature, the samples break. After the heat treatment (HT1), the recovery rate (considering the strain scale) is even lower, 2.39 % (Fig. 5a). The low degree of recovery rate at room temperature is explained as the result of the incomplete phase transformation, the alloy being partially in the martensite state, partially in the austenite state (A_f >35 ^{o}C). The recovery rate is higher at 60 ^{o}C, 4 % (Fig. 5b), due to the shape memory effect. After the stress was relieved, and the sample partially recovered at room temperature, the furnace was slowly heated until the sample fully recovered, based on the shape memory effect (Fig. 6 a, b). In this case, the total recovery rate was 6 %. The first type of heat treatment (HT1), for inducing two way shape memory effect, does not have an important contribution regarding the superelasticity.

The second type of heat treatment (the annealing) induced the superelasticity (Fig. 7. a, b, c). After cold rolling and annealing the samples did not show shape memory effect. The degree of superelasticity depends on annealing parameters (here, the temperature). According with our data, the superelasticty was increasing up to a point, after that it decreased. At 450 ^{o}C annealing temperature, the recovery rate was 7.5 %, but at 550 ^{o}C the recovery rate was just 3.25 %. The reason is that some processes related to recrystallization process occurred. It can also be assumed that there is a maximum recovery rate that can be obtained for a certain annealing temperature between 350 ^{o}C and 550 ^{o}C.

The plateau of stress-strain curves is explained as a result of reorientation of the martensite variants to a single orientation [5].

As preliminary studies, the results are considered helpful for understanding the complex characteristics of TiNi (50.6 at. % Ni) shape memory alloy. The authors consider the alloy proper for producing arterial stents, both self-expandable or superelastic. More studies are necessary for determination of the highest mechanical characteristics and recovery rate. The studies also helped to dissociate the effects of heat treatment on inducing the shape memory effect and the superelasticity.

5. Conclusions

1. In our research we studied some mechanical properties of TiNi (50.6 at. % Ni) shape memory alloy, using dynamic mechanical analysis and tensile tests.
2. The mechanical properties of TiNi (50.6 at. % Ni) strongly depends on heat treatment and processing history, as well as the testing temperature.
3. For those devices based on shape memory effect the difference between phase transformation temperatures indicated by DSC tests, and the stabilization temperature of mechanical properties should be considered.
4. The dynamic mechanical analysis and tensile tests are suitable and complementary methods for the investigation of phase transformations, beside differential scanning calorimetry.
5. As the present paper is a preliminary study of TiNi (50.6 at. % Ni) shape memory alloy, more advanced investigations are necessary, based on a complex design of the experiment, for pointing out the optimum parameters necessary for obtaining the highest recovery rate and an accurate control of phase transformation temperatures.

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[*] Corresponding author: dan_batalu@yahoo.com