EFFECT OF COLD WORK ON THE MECHANICAL BEHAVIOR OF NiTi

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ABSTRACT

The effect of cold work on the superelasticity, shape memory effect & hardness of NiTi alloy (51 atomic% Ni) is investigated in this paper. The as-received alloy, which was fully annealed at 850°C and had an austenitic structure at room temperature, was rolled at room temperature to reductions of 20%, 30% and 40%. Shape memory effect, nanohardness and superelasticity of the cold rolled samples were compared with the as-received material. Experimental results show that the shape memory recovery decreases with cold rolling and applied bending strain. Nanohardness values increase as thickness reduction increases. Superelasticity of cold rolled samples was generally lower than the as-received sample but increased with cold rolling. The observed results can be attributed to the presence of dislocations resulting from cold rolling, which increase the strength of the material and lead to martensite stabilization.

Keywords: NiTi, Cold rolling, Superelasticity, Shape memory effect, Nanohardness

INTRODUCTION

Shape memory alloys (SMAs) are considered a unique class of smart materials. According to Hodgson et al. [1], the shape memory property can be defined as the recovery of a predefined shape upon applying appropriate thermal treatment. The reason behind this behavior is the change from a martensite phase (low temperature phase) to an austenite phase (high temperature phase) with a predefined shape by heating. The thermomechanical behavior of the material changes according to temperature [1], with five main temperatures defining the behavior. These transformation temperatures are: $M_s$ and $M_f$ at which martensite starts to form and completes formation, respectively, $A_s$ and $A_f$ at which austenite starts to form and completes formation, respectively, and $M_d$ above which the material behaves as any ordinary material with no unique properties [2]. SMAs show their shape memory effect when the martensite phase is deformed and then heated to return to an austenite phase with a previous shape.

SMAs also show another unique behavior of superelasticity when deformed in their austenitic phase. When the austenite phase is deformed up to a certain strain level, martensite phase would be stress induced and upon removal of load the material...
would revert back to its austenitic phase recovering the original shape it had. The superelastic behavior occurs between the $A_f$ and $M_d$ temperatures when the material is fully austenitic and up to a certain strain level when slip occurs [1, 3, 4].

Among shape memory alloys, NiTi alloys have attracted much attention since their discovery. Compared to other SMAs, NiTi is much stronger and also tends to recover higher strains up to 8 or 10%. NiTi is also known for its biocompatibility and high corrosion resistance which has lead to its extensive use in medical applications in cardiovascular and orthopedic devices and surgical instruments [1,5]. In such applications, the $A_f$ temperature is a key optimization parameter that affects how a NiTi device is going to behave since it affects the stresses it exerts when implanted. According to Pelton et al. [6], the unloading stresses exerted by orthodontic Ni$_{50.8}$Ti$_{49.2}$ archwires deliver higher unloading stresses as the difference between the environment's temperature and $A_f$ increases, which can be painful.

Although several workers have investigated the effect of thermomechanical treatment on the behavior of NiTi alloys [7 – 15], little is known on the variation of their hardness, superelasticity and shape memory effect with cold work in the austenitic phase. The present work attempts to clarify these issues.

2. EXPERIMENTAL PROCEDURES

The shape memory NiTi alloy studied in this work has 55.8% Ni content by weight (50.7 at%) with the rest being Ti. The alloy was supplied by EUROFLEX GmbH, in the form of 1 inch diameter rod hot rolled and fully annealed at 800-850 °C. The transformation temperatures are $M_f = -53.7$ °C, $M_s = -38.9$ °C, $A_s = -33.5$°C and $A_f$ ranges from 5 to 18 °C. This means that the material is in its parent austenitic phase at room temperature. The rod was then cut into strips using wire EDM and the strips were given reductions in thickness of 20, 30 & 40% by cold rolling. The shape memory effect (SME), hardness, and superelasticity were measured for the different conditions.

Measuring SME was based on the ASTM standard F 2082-03 "Determination of Transformation Temperature of Nickel-Titanium Shape Memory Alloys by Bend and Free Recovery"[17]. The experiment was designed such that both the cold rolled and the as-received samples would be subjected to bending strain values of 2.5, 5 and 10% using the three point bending test. According to the equation

$$\varepsilon = \frac{T}{D},$$  \hspace{1cm} (2.1)

the choice of the sample thickness (T) and mandrels diameters (D) was made according to the desired bending strain values ($\varepsilon$).

According to the ASTM standard [16], alloys that are superelastic at room temperature should be tested in an alcohol bath of temperature of -55 °C or less using liquid nitrogen for cooling. This is to insure that the material would be loaded in its martensitic phase. To insure that the material has completely changed to martensite,
the loading was performed when the temperature has reached -70°C. This temperature was chosen to be lower than that specified by the standard since it has been noticed that cold rolled NiTi would have lower $M_s$ and $M_f$ temperatures [8,11].

After bending, the samples were removed from the fixture and the springback angle was measured, $\theta_{sp}$, without removing the samples from the cold bath. $\theta_{sp}$ was measured to be the angle between the two ends of the sample while still inside the cold alcohol bath. Then the samples were removed from the alcohol bath into the atmosphere, where the samples should recover back to the austenite phase, and the final angle reached after recovery was measured, $\theta_f$ as illustrated in fig 1. The shape memory recovery (SMR) was then measured as:

$$\text{SMR\%} = \left(\frac{\theta_f}{180}\right) \times 100$$  \hspace{1cm} (2.2)

An MTS XP nanoindenter was used to measure the nanohardness of the as-received and the cold rolled samples. Since the material under study is supposed to be superelastic, instrumented indentation techniques are more preferred than conventional optical techniques of measuring hardness that don't take into account elastic deformation[17]. A diamond Berkovich tip was used in order to measure nanohardness with 12-25 indents per sample. All indents were performed such that the nanohardness would be measured at the same depth in all samples (2000 nm).
using contact stiffness method (CSM) to eliminate the effect of depth variation. The nanohardness was taken as the maximum force divided by the area of contact.

Superelasticity is defined here as the ratio between the energy released from the material while unloading (E₂) to the energy stored while loading (E₁), as illustrated in fig. 2. This approach has been used to measure superelasticity in several studies [9, 18, 19]. In the present work, a tungsten carbide 400 microns diameter spherical tip and a diamond Berkovich tip were used to measure the superelasticity. For the Berkovich tip, a low load has been used (20 mN) based on research done by Liu et al [18], since significant difference in superelasticity of differently treated NiTi samples could only be found at 20 mN or less. This also agrees with Wood et al [20] since higher loads would mean higher strains that wouldn't probably be recoverable. As for the spherical tip, the maximum load of the nanoindenter was used (500 mN) to minimize surface roughness effects which increase with tip diameter and decrease with applied load [21].

![Fig. 2: Energies used for calculating superelasticity as E2/E1](image)

As-received and cold rolled samples were tested with 12-25 indents performed on each. Polynomial regression was used to find equations that fit both the loading and unloading curve of each indent since these curves are supposed to a polynomial relation [21]. The equations were then integrated and the ratio of area under unloading curve to area under loading curve computed to measure superelasticity.

3. RESULTS AND DISCUSSION

*Shape memory effect*

Shape memory recovery together with springback has been calculated for the as-received sample and the cold rolled samples according equation 2.2. Fig. 3 shows the effect of cold rolling on the shape memory recovery of the samples studied for each bending strain value applied.
Fig 3: Effect of cold rolling and bending strain on the shape memory recovery

Fig.3 shows that the shape memory recovery generally decreases with the cold rolling percentage and also with increasing the applied bending strain. As described in the experimental procedure, the shape memory recovery in the present study was measured by warming the alloy to room temperature, which is higher than the original $A_f$ temperature (5-18°C) of the as-received alloy. However, Lin et al. [8] have found that the $A_f$ temperature increases with the degree of cold rolling with an increment of about 120°C for a sample that was cold rolled to 40% thickness reduction. Similar result was observed by Hseih et al.[11], who found that the $A_f$ increased by about 250°C for a ternary TiNiZr shape memory alloy that was subjected to 25% thickness reduction. These findings can explain the decrease of shape memory recovery with cold rolling that was observed in the present study. It is expected that after the shape memory experiment some retained martensite would exist at room temperature. Martensite stabilization has been explained by Lin et al.[8] to be due to the dislocations that have been induced in the material due to cold rolling and that increase in density with the degree of cold rolling. These dislocations inhibit the martensite to austenite transformation by imposing friction stress on the interfaces between the two phases, which creates a higher energy barrier that needs to be overcome for the austenite phase to be completely formed. The decrease of recovery with the applied bending strain can also be explained in terms of the dislocations that form due to the applied bending strain and increase with the amount of bending strain applied as was also mentioned by Lin et al.[9] who have attributed the decrease in
recovery with increasing bending strain to the dislocations formed during the bending test.

Fig. 4 compares springback angle values for the as-received sample to the cold rolled samples for the three bending strain values.

![Graph comparing springback angle values for as-received and cold rolled samples](image)

Fig. 4: Chart comparing the springback angle value for as received and cold rolled samples for different bending strain values.

As can be seen in fig.4, the springback angle, $\theta_{sp}$, increases with cold rolling percentage for the same bending strain value applied. $\theta_{sp}$ also increases as the bending strain value applied decreases for the same cold rolling percentage. The three lines have been obtained using linear regression based on the springback angles that have been measured. The quality of fit is quite high with the R value being 0.983, 0.981 & 0.975 for the 2.5, 5 & 10% strained samples respectively.

Lin et al. [9] observed that cold rolled samples that are strained to a certain percentage would show lower residual strain, when unloaded, as the cold rolling percentage increases. Lower residual strain means more springback and so their results agree with what has been observed in this study. This is also in agreement with finding that the amount springback for most materials is found to be dependent only on the bend radius, for sheets with similar thicknesses, and to increase as the bend radius increases [22]. Since the amount of applied bending strain decreases with increasing bend radius according to equation (2.1), springback is also expected to increase with the decrease in applied bending strain.
Fig. 5: Charts showing both the springback and shape memory recovery angles for bending strain values of (a) 2.5 % (b) 5 % (c) 10 %
Fig. 5 shows that the shape memory recovery compared to the amount of springback increases with the amount of bending strain applied as is evident from the areas enclosed by the recovery and springback lines in the three charts. Fig. 6 shows that the ratio of shape memory recovery to springback increases with the amount of bending strain applied, which is what was noticed from fig. 5.

![Graph showing recovery to springback ratio](image)

**Fig. 6:** (Recovery/springback) ratio for different values of applied bending strain

**Nanohardness**

Nanohardness values that have been measured with the nanoindenter for all samples are represented in fig. 7.

![Graph showing nanohardness](image)

**Fig. 7:** Variation of nanohardness data with cold rolling
Polynomial regression was used to fit the nanohardness data values and the fit came out to be:

\[ H = 5.84 R^2 - 0.292 R + 3.865 \]  

(3.1)

with a correlation coefficient value of 0.996, where \( H \) is the hardness in GPa and \( R \) is \([(t_0 - t_1)/t_0]\), with \( t_0 \) and \( t_1 \) being the initial thickness and thickness after rolling, respectively.

From fig. 7, it is obvious that nanohardness values increase with the extent of cold rolling. These results agree with other studies that have measured the Vickers hardness of cold rolled NiTi and found out that hardness does increase with cold rolling percentage [8,10-12]. Since cold working is expected to create dislocations that increase the strength of the material, hardness is also expected to increase with increased cold rolling according to a direct proportional relation between hardness and yield strength [22].

**Superelasticity**

Fig. 8 shows the results obtained by using both the Berkovich and spherical tips. The results show that using both tips yields the same trend of data for the samples studied. The spherical tip yields higher values than the Berkovich tip although the Berkovich tip has been used with a lower load (20mN) than the spherical tip (500mN). Similar results have been observed by Wood et al.[20] who have observed significant difference in superelasticity between martensitic and austenitic NiTi when indented with a spherical tip than when indented with a Berkovich tip. This difference has been attributed to the high level of strains caused by the sharp conical Berkovich tip that is expected to suppress the superelastic behavior and cause more permanent strains than the spherical tip which causes smaller strains.

![Fig 8: Variation of average superelasticity (E2/E1) for the as received and cold rolled samples changing with cold rolling percentage using (a) Berkovich & (b) Spherical tips](image)
The dashed lines in fig. 8 represent the superelasticity value for the as-received sample which exhibits the highest superelasticity among all samples. The decrease in superelasticity of cold rolled samples compared to the as-received sample can be attributed to martensite stabilization, as discussed earlier. At room temperature, cold rolled samples are expected to have a certain amount of retained martensite phase and a smaller amount austenite phase than the as-received sample. Since the austenite phase is the phase that shows the superelastic behavior, those samples that aren't fully austenitic are expected to have lower superelasticity than the fully austenitic as-received sample.

Fig. 8 also shows that among the cold rolled samples, superelasticity increases with cold rolling percentage. Lin et al.[9] have observed similar results during tensile tests of 10% and 15% cold rolled samples loaded to the same strain value by measuring the areas under the loading and unloading curves. The reason behind this was also attributed to the strengthening effect, caused by cold rolling through formation of dislocations, that has increased the stress level required to cause slip. This would in turn lead to the material withstanding higher values of stress without slip occurring while martensite is being stress induced so superelasticity would occur up to higher values of stress [9,13,15].

Crone et al.[13-15] found that cold rolled NiTi samples subjected to tension tend to have a hysteresis stress value, the difference between the loading and unloading stress, that is significantly lower than as-received NiTi. This means that the unloading stress increases significantly with cold rolling to have a close value to the loading stress. This upward shift would mean that the area under the unloading curve would be higher than as-received NiTi. According to the definition used for superelasticity in the present study, this would mean that superelasticity does increase with cold rolling due to the upward shift in the unloading curve.

CONCLUSION

Austenitic NiTi shows an increase in nanohardness and a decrease in shape memory recovery with increasing cold rolling percentage. Superelasticity of cold rolled samples was generally lower than as-received NiTi but increased with increasing cold rolling. This behavior can be attributed to the dislocations that were introduced in the material during cold rolling. High hardness, which also means high strength, with the amount of cold work was achieved at 40% thickness reduction with no significant decrease in superelasticity. This could improve the performance of NiTi and extend its use in different applications that need both high strength and acceptable levels of superelasticity.
REFERENCES


