TECHNICAL ARTICLE

Short Duration Heat Treatments before Aging Increase Mechanical Hysteresis of Pseudoelastic NiTi Alloy

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High temperature (550 °C) and short duration (10, 15, 20 s) heat treatments were performed on pseudoelastic NiTi alloy in addition to the conventional aging process in order to increase the mechanical hysteresis of the material. Pre-treated and aged samples were compared with plain aged ones through mechanical testing, powder X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The introduction of the pre-treatment, in combination with the aging process, was shown to increase the mechanical hysteresis of the aged samples up to ~30% after stabilization. XRD analysis showed how the introduction of the pre-treatment introduces a recovery of the residual stresses in the material microstructure, as well as the nucleation of different sets of metastable precipitates (such as TiNi₃). We thus observe that the combination of pre-treatment and aging affects the alloys microstructure, causing a series of effects that synergise in increasing the material hysteresis.

Keywords mechanical properties, residual stresses, shape memory alloys, shape memory effect, thermomechanical processing

1. Introduction

Nickel Titanium (NiTi) alloy is a smart metallic material capable, like other shape memory alloys (SMAs), of undergoing a solid-state transformation between an austenitic and a martensitic phase. This characteristic is responsible for the two most known behaviors of NiTi: the shape memory effect and pseudoelasticity (Ref 1). Pseudoelasticity determines a nonlinear stress-strain relationship due to the transition from an initial austenitic state of the alloy, to the stress-induced martensite. The transition causes the appearance of a *plateau* with almost constant stress for a significant ($1.5\% < \epsilon < 10\%$) portion of the deformation (Ref 1, 2). If the applied stress is released, the material returns to its initial state, without any residual deformation, however the whole process is not completely reversible thermodynamically, as some energy is lost between the forward and reverse transformation, as highlighted by the difference of the stress levels between the loading and unloading *plateaux*. This hysteresis area is a major source of the damping capacity of NiTi, which allows it to find successful application in several fields where vibrations and dynamic loads are a matter of concern, such as civil engineering (Ref 3),

aerospace (Ref 4) or automotive industry (Ref 5). In all of these applications, the tuning and optimization of the pseudoelastic properties of NiTi are a crucial issue.

The mechanical properties of NiTi are determined by the alloy's chemical composition, and by the processing steps, which lead to the production of a component or device for the desired application (Ref 6). During its conventional processing, the SMA, after cold working (CW), is subjected to a thermal treatment (ageing) which affects its microstructure, determining its final thermo-mechanical properties (Ref 6, 7). The strengthening effect of cold working is maintained even in the aged material, increasing the *plateau* levels and improving cyclic stability. Higher levels of cold working also reduce the hysteresis area (Ref 8, 9).

The ageing process, which is usually conducted at temperatures around 1/3 of the melting point of the alloy, is generally optimized to induce a partial stress recovery in the material microstructure, as well as recrystallisation, and the formation of coherent metastable precipitates (Ni₄Ti₃), which have a strengthening effect (Ref 10). These precipitates stabilize the reversible stress-induced transformation, which in turn is responsible for the hysteretic behavior of the alloy (Ref 11, 12). The ageing treatment thus has to be sufficiently long to allow for the formation of this type of precipitates, but not excessively so, since overageing and excessive grain growth negatively affect the mechanical properties of the material (Ref 8, 9).

There is thus a trade-off between high mechanical performance (optimal pseudoelastic behavior) and a broad hysteresis, since the strategies that increase the hysteresis (e.g., lowering the initial cold work) also decrease the mechanical properties of the alloy (*plateau* level and cyclic stability). In the applications that seek to exploit pseudoelasticity (constant stress within certain deformation ranges), it is usually desirable to have high *plateaux* levels and a narrow hysteresis (Ref 13). However, if the aim is to exploit the damping properties of NiTi together with pseudoelasticity, alternative strategies to maintain good

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mechanical properties while expanding the hysteresis would be welcome.

The present work aims at investigating a different strategy for tuning the hysteretic behavior of pseudoelastic NiTi, by altering the conventional processing steps in order to address the previously described trade-off. Our approach is to introduce a preliminary treatment, after the cold-working process and before ageing. This pre-treatment is characterized by a relatively high temperature (1/3 of the melting point instead of 2/3) and a short duration (~ 10 s). The aim of the pre-treatment is to induce a partial stress recovery in the material, and affect its microstructural evolution during the ageing process, thus increasing hysteresis levels without negatively affecting the mechanical performances. To the best of our knowledge, such an approach has not been described before for pseudoelastic NiTi.

The paper is organized as follows. In the Materials and Methods section we describe the selected alloy and the thermo-mechanical processing investigated, as well as the characterization techniques used to determine the pre-treatment effects. We then present the Results of our analysis, and, in the Discussion, we propose an explanation for the effects of the proposed pre-treatment on the microstructural phenomena during ageing, and how these in turn affect the hysteresis of NiTi. Finally, we draw our Conclusions.

2. Materials and Methods

2.1 Material Selection and Thermomechanical Treatments

Commercial nickel-rich NiTi with a nominal composition $\text{Ni}_{50.6}\text{Ti}_{49.4}$ was obtained for this study. The material was received as a 1.2 mm diameter wire in the cold-worked state. The wire was then cold drawn to a nominal diameter of 0.4 mm, with residual cold-work level of 43% (cross-sectional reduction). Several samples were then cut from this wire, and subjected to pre-treatments at high temperature ($T=0.4T_m = 550^\circ\text{C}$, where $T_m=1300^\circ\text{C}$ is the melting temperature for NiTi) for a set of short durations (10, 15, 20 s). During both the pre-treatments and the subsequent ageing process (straight annealing), the samples were constrained within an *ad hoc* fixture, which applied a 3% pre-strain to the wire, in order to set its shape.

After the pre-treatments were completed, we used a method we developed in a previous work (Ref 9) to estimate the optimal duration for the ageing of the pre-treated samples, and an additional sample that had not undergone any pre-treatment. Briefly, we used electric resistance measurements to determine a latency (the D point) where the voltage signal acquired from the sample during annealing starts to decrease after a trough and a plateau.

Ageing was carried out in an electric kiln at 435°C .

As reported in Fig. 1, our measurements showed that there was no significant difference for the optimal ageing duration between the various samples. Therefore, ageing duration was set to 400s for all samples. The process, comprising the pre-treatment (with the selected durations) and the ageing, was repeated identically for three different sets of samples, in order to be able to verify the repeatability of the ensuing mechanical testing results.

2.2 Mechanical Testing

A set of quasi-static (strain rate = $0.02\%/s$) tensile tests (ElectroPuls E3000, Instron, Norwood, Massachusetts, USA) was conducted, starting from a 1% maximum strain, and increasing this level progressively by 1% up to 5%. Then, 50 stabilization cycles at 0.05Hz and 5% strain were applied. The quasi-static tests were then repeated after the stabilization.

All the mechanical tests (quasi-static before stabilization, stabilization, quasi-static after stabilization) were carried out at room temperature (25°C) and were repeated three times for each condition, i.e., plain aged, and pre-treated-and-aged (pre-treatment at 10s, 15s and 20s).

The hysteresis area of the stress-strain curves was calculated as the difference between the areas under the loading and unloading curves.

2.3 Diffraction and Calorimetric Measurements

For the powder X-ray diffraction (XRD) experiments, segments cut from the samples were mounted in resin, mechanically ground and polished. XRD was carried out at 25°C in the $30\text{--}120^\circ 2\theta$ range with a Bragg-Brentano set-up (PANalytical X'Pert PRO MPD, Almelo, The Netherlands) using $\text{Cu K}\alpha$ radiation. Employing a spinner sample stage for positioning, the measurements were repeated for two values of φ (yaw around sample surface normal), i.e., at $\varphi=0^\circ$ (incident beam in a plane parallel to the NiTi wire), and $\varphi=90^\circ$ (orthogonal).

XRD spectrum analysis for pattern fitting and the determination of the phases was carried out using a Rietveld analysis software (MAUD 2.94, Luca Lutterotti (Ref 14)). The *a-priori* crystallographic data for the B2 (Ref 15) and R phase (Ref 16), as well as Ni_4Ti_3 (Ref 17) and TiNi_3 (Ref 18) were taken from the literature.

Differential scanning calorimetry (DSC) (DSC Q100, TA Instruments, New Castle, DE, USA) was also conducted on the samples. A cooling and heating ramp between 125 and -150°C , and back to 125°C , was applied at $\pm 15^\circ\text{C}/\text{min}$.

3. Results

3.1 Mechanical Testing

Mechanical tests were carried out on the pre-treated and aged samples, as well as the sample that was only subjected to the ageing process (we shall refer to it as “plain-aged sample”).

All the samples tested show a typical pseudoelastic behavior with the corresponding hysteresis gap between the upper (loading) and lower (unloading) transformation plateaux. The mechanical characteristics underwent very limited ratcheting during cycling, thanks to the optimized ageing process. All samples had a stable behavior after 50 cycles at 5% strain. No relevant differences in this respect were observed between the plain-aged and pre-treated-and-aged specimens.

Otherwise, the tensile tests do highlight several differences between the plain-aged and pre-treated samples. Figure 2 shows an example of the results obtained from NiTi samples after 50 stabilization cycles. Notice that, this set of curves was chosen because it is particularly representative, but all the phenomena that we will discuss were observed in every set of mechanical tests, both before and after stabilization.

Fig. 1 Electric resistance measurements to determine optimal ageing duration, highlighted by point D. A full description of the experimental protocol and its rationale can be found in (Ref 9).

Fig. 2 Stress-strain curves for plain aged and pre-treated-and-aged samples at various levels of maximum strain. The curves refer to the stabilized condition (after 50 stabilization cycles).

First of all, the pre-treatment appears to cause a stiffening of the material, increasing with the duration of the treatment. This effect is evident when comparing the linear elastic trait of the stress-strain curve for the test at 1% strain.

Additionally, the pre-treatment also causes the insurgence of more significant Lüders-like phenomena, as is clearly visible in the 5% strain curves.

Finally, the pre-treatment also affects the *plateau* levels. As pre-treatment duration increases, both loading and unloading *plateau* stresses rise. Regardless of pre-treatment duration, the loading *plateau* is always higher for the pre-treated samples than for the plain aged samples. Moreover, at 20s there is a lowering of the unloading *plateau*, i.e., down

to stress levels comparable to those characteristic of the plain aged sample. Such a change affects the hysteresis loop size.

In general, pre-treated samples display a higher hysteresis than the plain aged ones. The highest hysteresis increase is obtained for the 20s sample (+29.4% after stabilization). This effect is clearly visible in Fig. 3, where boxplots of the hysteresis values measured for all the different sample sets have been collected.

3.2 XRD and DSC

XRD measurements were conducted on the plain-aged, pre-treated (only), and pre-treated-and-aged samples, in particular with pre-treatment duration 20s. Pre-treatment affects the microstructure of the samples in several respects (Fig. 4). Comparing the

Fig. 3 Distribution of hysteresis values for all mechanical tests carried out on plain-aged and pre-treated-and-aged samples. On the left, hysteresis values before stabilization. On the right, hysteresis values after stabilization

Fig. 4 XRD analysis of plain aged, pre-treated (20s) and unaged, and pre-treated (20s) and aged samples (all spectra background-subtracted and normalized at 100 for the height of the most prominent peak). Top: full spectrum at $\varphi=0^\circ$ – the reduced presence of R phase reflections in the pre-treated samples highlighted, as well as B2 reflections. Bottom left: detail of the $\varphi=0^\circ$ spectrum in the $37\text{--}48^\circ 2\theta$ range, with precipitates and R phase reflections highlighted. Bottom right: detail of the spectrum within the same 2θ range, but at $\varphi=90^\circ$

plain-aged with the pre-treated-and-aged samples, it appears that the prominence of the reflection peaks associated to B2 phase (Austenite) remains largely unaffected by the pre-treatment. The same cannot be said about the occurrence of the rhombohedral (R) phase, which is present in the plain-aged samples, but markedly reduced in the pre-treated-and-aged ones, as shown by the low intensity of R phase reflections in the region $44\text{--}55^\circ 2\theta$. The R phase also displays a φ dependence, as for both pre-treated-and-aged and plain-aged samples, the R phase reflections are mostly visible at $\varphi=0^\circ$.

Especially in the $37\text{--}48^\circ 2\theta$ range, XRD also shows that the 20s pre-treatment causes the nucleation and growth of different metastable precipitates. While the plain-aged sample displays reflections associated to Ni_4Ti_3 , the pre-treated-and-aged one shows lower concentrations of this precipitate. On the other hand, 20s pre-treated samples show the presence of TiNi_3 ($2\theta = 38.34^\circ$) after ageing, which is absent from the plain-aged sample.

In the $37\text{--}48^\circ 2\theta$ interval (and in the whole spectrum), it is also possible to observe that the B2 reflection peaks for the pre-treated-only (unaged) sample are narrower when compared to the other two samples, while the reflections associated to the various precipitates are generally absent. The R phase reflections are present in this sample, but have the lowest intensity of all of the three samples.

DSC measurements (Fig. 5) show that the transformation temperatures are not affected by the introduction of the pre-treatment, as there is no significant difference between the temperatures of the plain aged sample and the pre-treated and aged one.

4. Discussion

4.1 Pre-treatment Effects on the R Phase

Both mechanical and XRD measurements seem to concur in showing that the introduction of the pre-treatment affects the

evolution of the R phase during the thermomechanical processing of the alloy.

It is reasonable to assume that the relatively high temperatures of the pre-treatment induce the desired partial stress recovery in the crystalline lattice, even with short treatment durations. This is consistent with the absence of a characteristic strain-hardening-related peak broadening in the pre-treated-only specimens. Also, it is proven by the electric resistance measurement in Fig. 1, where the initial minimum (stress recovery) occurs earlier and for lower voltages (resistances) in the pre-treated samples. This micro-stress recovery may contribute, together with the different sets of precipitates (as we will discuss in Sect. “4.3”), to the inhibition of the R phase observed after the ageing process (Ref 2). This is confirmed in our samples by the XRD measurements: reflections associated to the R phase are, in fact, almost absent from the pre-treated samples. The reduced presence of R phase can explain the stiffening of the material observed in the mechanical testing, as well as the rise in the level of the loading plateau.

4.2 φ -Dependence of the R Phase Reflection Intensity

The R phase displays a φ -dependence in the XRD spectra of the plain-aged sample. This can be explained by the pre-strain introduced during the cold-working of the wire, which is likely inducing a preferential orientation for the formation of this phase.

4.3 Pre-treatment Effects on Microstructural Evolution

Focussing on the characteristics of the B2 phase, the introduction of the pre-treatment does not seem to alter its final characteristics, as indicated by similar XRD peak intensity, shape, and position, as well as its transformation behavior, in as much as DSC-measured transformation temperatures are rather similar, irrespective of the pre-treatment.

On the other hand, the combination of pre-treatment with conventional ageing appears to introduce some relevant effects

Fig. 5 Comparison of DSC measurements for the plain-aged and the pre-treated (20s) and aged samples

in the evolution and stability of the secondary phases. XRD measurements on the 20s (no ageing) sample show a reduced level of pre-strain (narrower B2 peak). This can be explained by the pre-treatment causing a recovery of the residual stress in the microstructure, and possibly inducing a partial recrystallization with a decrease in the number of dislocations. This different starting condition is likely promoting the formation of alternative sets of precipitates during the ageing process. While coherent metastable precipitates (in particular Ni_4Ti_3) are still produced even after pre-treatment, as shown once again by XRD measurements, the pre-treated and aged samples exhibit higher concentration of TiNi_3 than the plain-aged ones. A larger proportion of incoherent equilibrium precipitates, together with a reduced density of dislocations, as we previously discussed, can be at the basis of the reduced stability of the R phase (Ref 2), and the consequent rise in the plateau levels displayed by the pre-treated and aged samples.

Through the reduction in localized stress concentrations, the pre-treatment may also promote a more homogeneous formation of Ni_4Ti_3 (Ref 19, 20). A finer dispersion of Ni_4Ti_3 can be another contributing factor to the strengthening effect caused by the combination of pre-treatment and ageing, as shown by mechanical testing.

Tensile tests also show a lowering of the unloading plateaux for the 20s pre-treated and aged sample. This could be attributed to the asymmetric influence of coherent precipitates on the stability of the two-step transformation, with a minimal impact on the $\text{B2} \rightarrow \text{R}$ and a moderate impact on the $\text{B19}' \rightarrow \text{R}$ transitions (Ref 8). A proportional increase in TiNi_3 vs. Ni_4Ti_3 may thus have a stronger abating effect on the unloading than the loading plateau stress, so that the former fails to rise as much as the latter as a consequence of the better Ni_4Ti_3 dispersion. With this in mind, we can explain why the unloading plateaux of the 20s sample is lower when compared to the 10s and 15s: with a longer duration of the pre-treatment at high temperature, a larger amount of TiNi_3 can be nucleated, which will grow during ageing, ultimately determining a larger disproportion of incoherent vs. coherent secondary phases.

Finally, the combination of the overall stiffening and strengthening of the material during loading, with the lowering of the unloading plateaux in the 20s sample, produces a relative gain in the hysteresis of up to 30%.

Our method, while successful, has some limitations. In particular, the brief durations of the pre-treatment make it challenging to achieve highly repeatable results, and make the process quite sensitive to the experience of the operator managing the treatments. This effect is particularly evident in the 10s pre-treatment, where pre-treatment duration is comparable to the duration of the operations of insertion into the kiln, extraction, and quenching. Consequently, the standard deviation of the hysteresis gain caused by the pre-treatment increases as treatment duration decreases.

This issue may be addressed by investigating the effects of pre-treatment temperature, instead of just duration, and verifying whether it is possible to achieve similar effects to the 550 °C treatment in a longer time by slightly decreasing temperature.

5. Conclusions

The aim of the present work was to address the trade-off between high hysteresis and mechanical performance present in the conventional process to optimise pseudoelastic NiTi. By

introducing, after cold working but before aging, a preliminary heat treatment at high temperature ($T = 550$ °C) and short duration ($t = 20$ s) we managed to successfully increase the mechanical hysteresis of the material. We also obtained higher stiffness of the linear elastic trait of the deformation, and higher loading plateau levels, without compromising the cyclic stability of the material. We explained these effects by highlighting how the pre-treatment modifies the evolution of the forward and reverse two-step transformation, and ultimately affects plateau levels and increases the overall hysteresis, by promoting a different formation of precipitates.

In conclusion, introducing our suggested pre-treatment can lead up to a 30% gain in hysteresis without loss in cyclic stability and with improved mechanical performance, effects which will undoubtedly prove very significant in the various applications where NiTi is chosen for its damping capacity.

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