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The Effects of Cold Work and Heat Treatment on the Properties of Nitinol Wire

Masao J. Drexel and Guna S. Selvaduray
San Jose State University, San Jose, CA, USA

Alan R. Pelton
Nitinol Devices and Components, Fremont, CA, USA

ABSTRACT

The successful medical application of Nitinol requires precise control of its transformational and mechanical properties. In this study the effects of heat treatments at 300-550°C for 2-180 minutes on Ti-50.8at%Ni wire with 30% and 50% initial cold work were investigated. Transformational and mechanical properties were characterized through the BFR technique and tensile testing. Thermally activated precipitation and annealing processes were observed. Annealing processes tended to increase the maximum slope of the BFR curves. The R-phase was observed with greater frequency and prominence in the 50% cold-worked wire after heat treatment. The general trends in A_f are summarized in two TTT diagrams; both illustrate a maximum precipitation rate of Ni_4Ti_3 at 400-450°C. The trends in tensile properties are outlined for all heat treatment conditions. Recovery processes occurred at all temperatures. The onset of recrystallization occurred at approximately 450°C for both wires.

INTRODUCTION

Since its discovery in the early 1960s Nitinol has attracted an increasing amount of attention. A near room-temperature phase transformation results in shape-memory and superelastic properties, which allow Nitinol to provide functionality never possible with conventional engineering alloys [1]. Additionally, the good biocompatibility of Nitinol has allowed it to be successfully used in a variety of biomedical devices [2]. Devices such as stents, *vena cava* filters, and endodontic files (shown in Fig. 1) all place unique demands on the material. The successful application of Nitinol requires precise control of both transformational and mechanical properties. Ultimate tensile stress (UTS), upper plateau (UP) stress, lower plateau (LP) stress, and austenite finish temperature (A_f) are some of the relevant properties. These properties can be adjusted, through careful processing, to optimize performance for a given application.

Heat treatment is the most common process used to tailor the properties of Nitinol. During aging, the nucleation and growth of Ni-rich precipitates has been well documented and is commonly used to increase the A_f for Ni-rich compositions [3,4]. These precipitates have also been observed to act as effective barriers to dislocation motion, thus strengthening the alloy [4]. Furthermore, the strain fields introduced by precipitates can act to stabilize the rhombohedral or 'R-phase' resulting in two-stage transformation [5,6].

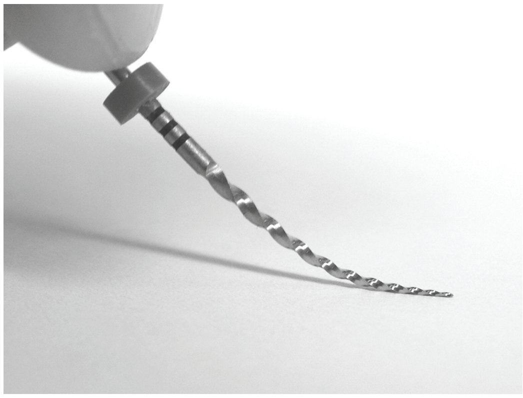

Figure 1: Bent Nitinol endodontic file.

Heat treatments that provide the thermal energy required for precipitation can also activate the processes of annealing, during which the rearrangement of defects and the decrease in defect density removes the stored strain energy within the lattice. These processes affect both the thermal and mechanical properties. The driving force for annealing is greater in more heavily cold-worked metals due to their higher amount of stored internal energy [7]. Therefore, the response to heat treatment depends on the processing history, time, temperature, and amount of cold work.

OBJECTIVE

This study was undertaken to outline the trends in the transformational and mechanical properties of as-drawn Nitinol wire, with 30% and 50% initial cold work, during heat treatment at a range of typical processing temperatures where precipitation, recovery, and recrystallization occur.

EXPERIMENTAL METHODOLOGY

Ti-50.8at%Ni wires with 30% and 50% cold work at a final diameter of 1mm were studied. Heat treatments were performed in a salt bath followed by a water quench. A summary of the heat treatment temperatures and times is given in Table 1.

Table 1: Heat treatment conditions

Temperature (°C)	Time (min.)
300, 350, 400, 450, 500, 525, 550	2, 5, 10, 20, 60, 180

The transformational properties were characterized by the bend and free recovery (BFR) technique in accordance with ASTM F 2082-03. This test involves cooling the wires in an alcohol (or water) bath to stabilize the martensite phase. A temperature of -70°C was usually sufficient in this study. The wires were then strained 2-2.5% and their recovery was monitored during heating. Due to the high levels of cold work and the R-phase present in many of the specimens tested in this study the A_f was not determined by the intersection of tangent lines. Instead A_f was identified as the point where displacement ended. Three specimens were tested for each heat treatment and cold work condition.
Tensile properties were characterized by ASTM F2516-05, which consists of loading the specimen to 6% strain, unloading to a stress of 5MPa, and then loading to failure. To avoid

temperature effects, a strain rate of 0.06 in/min (~1.5 mm/min) was utilized in this study. Testing was performed at room temperature.

TRANSFORMATIONAL PROPERTIES

BFR testing was attempted with both the as-drawn wires and after heat-treatment at 300°C. However, even after cooling to below -100°C the springback of these wires was so significant that testing could not be performed.

The increase in A_f resulting from the formation of Ni-rich precipitates is observable throughout the BFR plots. The time-temperature-transformation (TTT) diagram constructed by Nishida *et al.* had established that at the temperatures of 500-800°C the precipitation sequence of $Ni_4Ti_3 \rightarrow Ni_3Ti_2 \rightarrow Ni_3Ti$ occurs [3]. As the Ni concentration in the surrounding matrix is depleted during precipitation, the transformation temperature increases with increasing heat treatment time, as illustrated in Fig. 2, for both 30% and 50% cold-worked wires. Note that the shape of the low-temperature BFR curves do not significantly change with increased heat treatment time. However, higher temperature heat treatments do change the shape of the BFR curves, due to annealing, and stabilization of the R-phase; these processes tend to interfere with the trend of increasing A_f, as illustrated in Figs. 3 and 5. The higher level of residual cold work present in the 50% cold-worked wire was found to flatten the corresponding BFR curves in Fig. 2. A comparison of the BFR curves in Figs. 2 through 4 illustrates that with increasing heat treatment temperature, and time at the higher temperatures, the maximum slope of the BFR curves increases. This indicates that the austenite-martensite transformation proceeds more readily as the internal stresses introduced during cold work are released as a result of annealing.

The trend of increasing A_f of the 50% cold-worked wire is seen to temporarily pause during heat treatment of 2-20 minutes at 450°C, seen in Fig. 3. This pause is the result of the annealing processes that cause a shortening of the tail of the BFR curve. The reduction in the tail length effectively neutralizes the increase of the A_f. These observations illustrate the interplay between the precipitation reaction and the annealing processes. This pause in the increase of A_f can also be observed in Fig. 5.

The presence of the R-phase is clearly observed in Fig. 3. A comparison of the 30% and 50% cold-worked BFR curves shows that the R-phase is stabilized after only two minutes of heat treatment at 450°C in the 50% cold-worked wire. At times of 2-20 min.

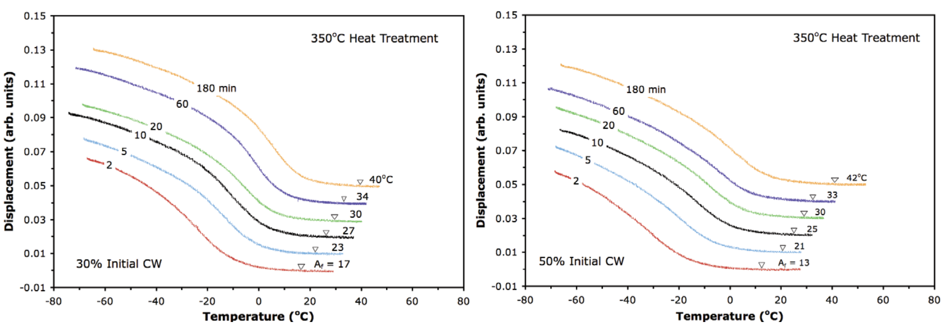

Figure 2: BFR curves for 30% and 50% cold-worked Nitinol wires after heat treatment at 350°C.

the R-phase flattens the 'tail' of the recovery curve. Longer heat treatments result in a typical two-stage transformation. In the 30% cold-worked wire, however, the R-phase is only observed after heat treatment for 20 minutes. This supports previous studies, which reported that the R-phase is stabilized by cold work [5,6,8].

Following heat-treatment for 2-10 minutes at 550°C the wires are observed to posses lower A_f values, shown in Fig. 4. The decrease in A_f at these high temperatures has been addressed in a study by Pelton *et al.* who explained that 300-500°C heat treatments result in the formation of the Ni_4Ti_3 precipitate; heat treatments at 500-600°C, however, result in the dissolution of the Ni_4Ti_3 precipitate followed by the eventual formation of the Ni_3Ti_2 and Ni_3Ti precipitates [4]. The initial dissolution process increases the Ni concentration of the matrix thereby decreasing the A_f. This is observed as the low A_f values for heat treatments of 2-20 minutes at 550°C. The rapid increase in A_f during heat treatments of 20-180 minutes, seen in Figs. 4 and 5, is attributed to the efficient Ni depletion resulting from formation of the Ni_3Ti_2 and Ni_3Ti precipitates.

Also interesting to note is the unique shape of the BFR curves obtained after heat treatment at 550°C for 60 minutes for wires with both levels of cold work. Similar curves were also obtained after heat treatments of 180 minutes at 525°C. These curves are distinguished by a sharp transformation onset followed by a slow end – a long tail. The cause of these curves shape is not known but it is suspected that the shape of these curves may result from a point in the precipitation process where the precipitate-matrix coherency strains are at a maximum. This unique transformation behavior is also noted to disappear with continued thermal input suggesting it results from a transient microstructure obtained during heat treatment.

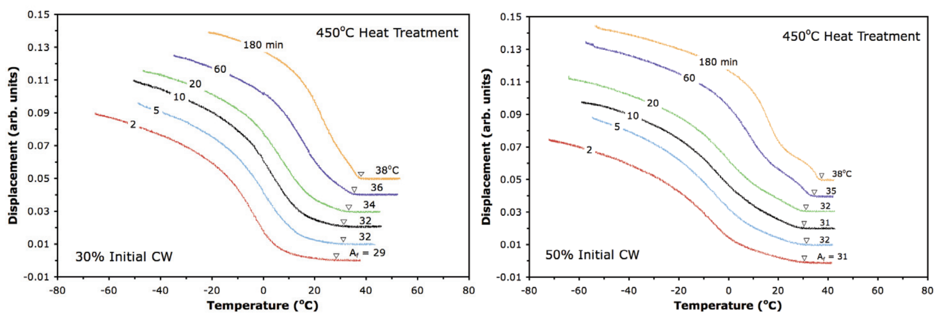

Figure 3: Representative BFR curves for 30% and 50% cold-worked Nitinol wires after heat-treatment at 450℃.

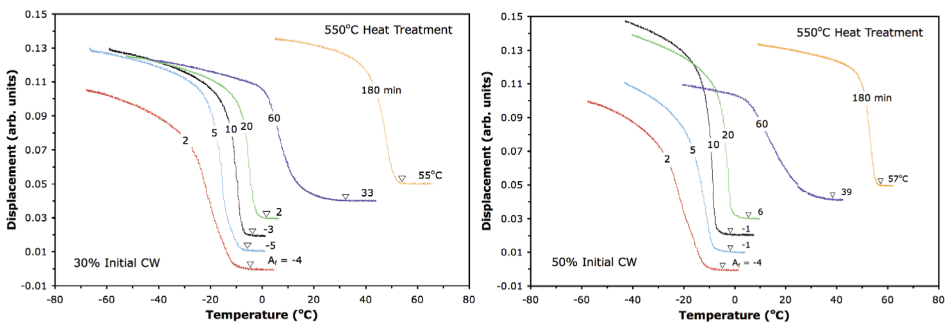

Figure 4: Representative BFR curves for 30% and 50% cold-worked Nitinol wires after heat-treatment at 550℃.

Summaries of the trends in A_f for all heat treatment temperatures, and for each level of cold work, are shown in Fig. 5. A comparison of the two A_f versus heat treatment time plots shows that the general trends in A_f are similar for the samples of both levels of cold work. At short times the intermediate temperatures of 400-450°C are the most effective at increasing the A_f of the wires, due to the maximum precipitation rate of Ni_4Ti_3. At longer times the highest heat of Ni from the matrix during formation of the higher Ni concentration Ni_3Ti_2 and Ni_3Ti precipitates.

The only significant effects of cold work on the A_f occur at the intermediate temperature range of 400-450°C. Here the more heavily cold-worked wire has a higher A_f at short heat treatment times as a result of the long BFR tails. Interestingly, this temperature range falls very close to the temperatures commonly utilized in A_f tuning processes and therefore these differences are relevant when processing medical devices.

The general trends in A_f during heat treatment are illustrated in Fig. 6 as two TTT diagrams. These two diagrams show the increase in A_f at 400 and 450°C as a shift in the nose to the left. This shift corresponds directly to the long tails of the 50% cold-worked BFR curves seen in Fig. 3. It should be noted that these diagrams were constructed from a small number of points and are therefore only intended to illustrate the general trends in A_f increase – hence the dotted lines. As previously noted by Pelton the shape of the TTT diagrams results from the balance between the nucleation and growth phenomena [4]. At high temperatures diffusion rates are high but the driving force for nucleation is low while at lower temperatures the reverse is true. Therefore, it is at intermediate temperatures where the combination of the nucleation and growth rates are maximized, resulting in a maximum rate of A_f increase.

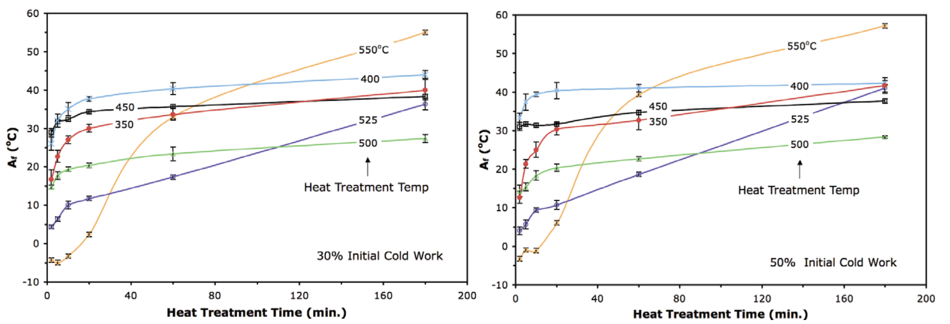

Fig. 5: Trends in A_f of 30% and 50% cold-worked Nitinol wires during heat treatment at a range of temperatures.

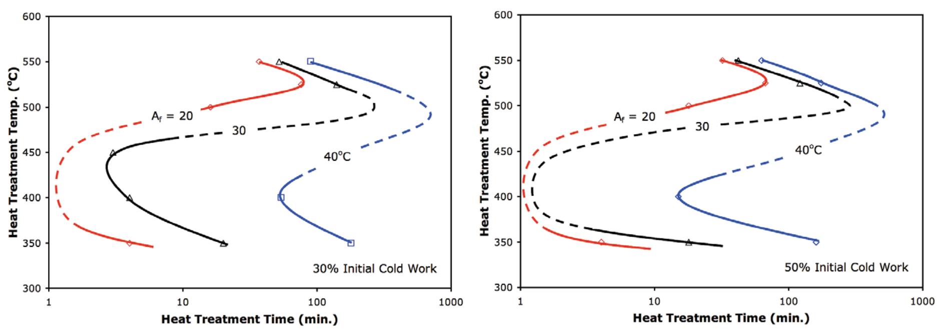

Figure 6: Trends in A_f of 30% and 50% cold-worked Nitinol wires during heat treatment at a range of temperatures.

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