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Abstract

The austenite transformation finish temperature, A_f, has been specified as a key characteristic in product specifications for an increasing number of Nitinol medical devices. Many literatures also interpret the A_f temperature as a sole parameter for predicting the Nitinol material properties. As a result, the industry is spending a significant amount of resources to test this transformation temperature as a means for product quality assurance. In the present study, cold drawn wires of Ti-55.8wt%Ni alloy were heat treated at a temperature of 350-600°C for durations up to 120 minutes. Mechanical properties were determined by tensile tests while the transformation temperatures were measured by differential scanning calorimetry (DSC) and bend and free recovery (BFR). The fatigue properties of selective specimens were also evaluated using a rotating beam fatigue test method. The purpose of the study is to evaluate the correlation between tensile mechanical properties and the A_f temperatures measured using the various techniques. The results will also assess the influence of Af temperature on Nitinol fatigue life.

Key Words

Transformation temperatures, A_f temperature, differential scanning calorimetry, bend and free recovery test, mechanical properties, rotating beam fatigue test

Introduction

Nitinol alloys when fully recrystallized after annealing at elevated temperatures greater than 600°C exhibit a single stage martensitic transformation from the parent B2 to B19' monoclinic martensite. However, for most medical devices and implants the Nitinol alloy is optimized for superelastic mechanical properties by cold working and subsequent heat-treatment at lower temperatures such that nano-sized subgrains, high density of dislocation and very fine Ni-rich precipitates are present in the material [1]. Transformation in this type of microstructure generally proceeds in two stages of B2 $\rightarrow$ R-phase $\rightarrow$ B19' martensite.

Defining the alloy formulation by specifying one of the transformation parameters measured by differential scanning calorimetry (DSC) of a fully annealed material is straight forward because hysteresis and transformation kinetics are relatively constant for a well defined microstructure [2]. However, defining the mechanical properties by specifying one of the transformation parameters of a heat treated but not fully recrystallized alloy can be quite challenging because of the following issues:

key parameter for specifying Nitinol devices [3]. The Food and Drug Administration (FDA) also endorsed this approach in its guidance for non-clinical tests for intravascular stents [4]. It is however recognized that materials having a constant A_f temperature may exhibit different mechanical and even different transformation characteristics [5].

Several factors can influence the temperatures of transformation (TTR). In a study on heat treating an equiatomic NiTi alloy, Thoma et al [6] found that increasing reduction of cold work and lowering heat treat temperature always elevate the R-phase to austenite TTR but generally suppress the martensitic to austenite TTR. However, at low cold work reductions, the trend on the martensite to austenite TTR reverses to higher temperatures with lower heat treat temperatures. The martensitic transformation hysteresis is widened by increasing cold work and decreasing heat treat temperature, but the R-phase hysteresis is less sensitive to cold working or heat treat conditions. For Ni-rich compositions such as those commonly used for superelastic medical devices, precipitation of Ni-rich phases during heat treat elevates TTR as the matrix becomes depleted in Ni [7].

To further clarify the validity of using the A_f temperature for specifying Nitinol devices, the present study investigated the effects of heat treatment on mechanical properties and the A_f temperatures measured by both DSC and Bend and Free Recovery (BFR) methods. A group of specimens having a constant A_f temperature was used for assessing their differences in plateau stresses, ultimate tensile stresses (UTS) and fatigue endurances.

Experimental

Cold drawn Ti-55.8wt%Ni wires of 0.020" in diameter were used for the present study. The as-drawn wires having an UTS of 257 Ksi were heat treated in a temperature range of 350-600°C for various durations up to 120 minutes. Mechanical properties were determined by tensile tests at 37°C while the TTR as defined in ASTM F2005-05 [8] were measured by differential scanning calorimetry (DSC) [9]. The functional A_f temperature was determined by a bend and free recovery (BFR) method of ASTM F2082-03 [10] in which procedure the test specimen was bent at -60°C before measuring the shape recovery on heating. The fatigue endurances of selective specimens with an as-drawn, heat treated surface finish and a BFR A_f in the range of 27+/-2°C were studied using a rotating beam (RTB) fatigue test apparatus in a 37°C water bath.

Results and Discussion

DSC Transformation Temperatures

DSC scans from 70°C to -100°C of specimens heat treated at 350-400°C did not detect any transformation with the only exception of R-phase peaks exhibited by the specimen heat treated at 400°C for 120 minutes, the TTR of which are R_s=49°C, R_f=26°C, A_s=33°C and A_f=52°C.

For specimens heat treated at 450°C, the DSC scans detected primarily the R-phase transformation. The TTR are plotted in Figure 1. Both R_s and A_f decrease while R_f and A_s increase rapidly with heat treat time signifying that the width of the transformation peak is becoming narrower and better defined with increasing heat treat duration as the cold work deformation is quickly annealed out. Although no martensitic peak was detected on cooling, the minutes is very much similar to that of those heat treated at 450°C but with the R-phase transformation occurring at a lower temperature range. The transformation of those heat treated for extended durations longer than 30 minutes is characterized by split cooling and heating peaks, hence M_s, M_f, R_s' and R_f' can all be determined. Again, the TTRs increase with prolonging heat treat perhaps due to the increasing amount of Ni-rich precipitate. The hysteresis for both R-phase and martensite also decrease with time.

DSC TTR of those heat treated at 550°C are plotted in Figure 3. The results are characterized by separated cooling peaks and a merged single-stage reverse transformation. The cold work strain appears to be annealed out very rapidly within the first few minutes as the R_s and R_f quickly stabilize followed by rapid rises of all TTR due to the Ni-rich precipitation. The martensite hystersis narrows expeditiously as the material approaches the fully annealed state with time.

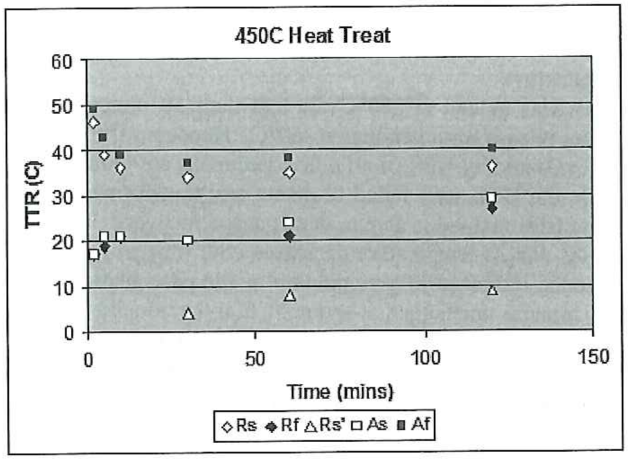

Figure 1: DSC TTR of specimens heat treated at 450°C.

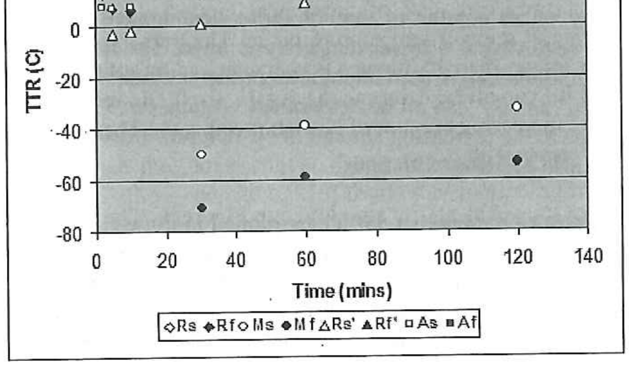

Figure 2: DSC TTR of specimens heat treated at 500°C.

BFR A_f Temperature

For specimens heat treated at 350°C for less than 30 minutes substantial superelasticity was observed during release from bending at -60°C. Hence no BFR A_f could be determined. The A_f temperatures measured by BFR of all other specimens are plotted in Figure 4. It is interesting to note that while the DSC scan failed to detect any transformation for specimens heat treated at 350-400°C, the BFR method is able to detect shape recovery. During 350°C heat treat for longer than 30 minutes, the A_f temperature decreases with time, suggesting that the annealing effect is dominant over the influence of precipitation as the precipitation kinetics is slow at 350°C. At 400°C, the A_f remains unchanged at about 20°C and gradually increases during the extended heat treat duration while at 450°C, the A_f is relatively constant for up to 120 minutes. The constant A_f over a period of heat treat duration may be caused by the balancing effect between annealing and the precipitation of Ni-rich intermetallics. The trends of BFR A_f are generally consistent with those of the DSC A_f.

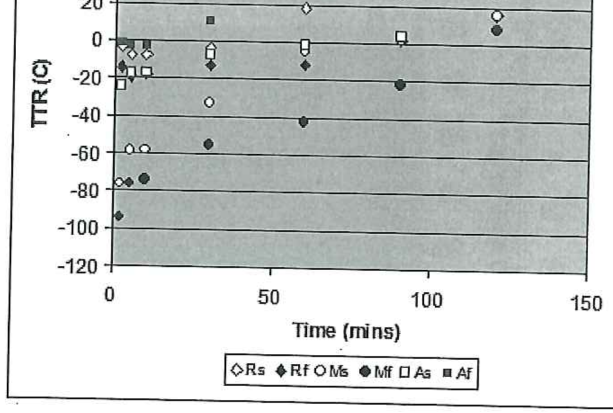

Figure 3: DSC TTR of specimens heat treated at 550°C.

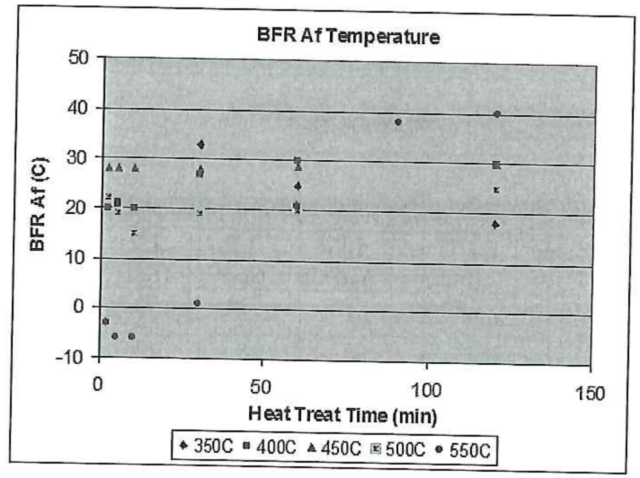

Figure 4: The A_f temperatures determined by BFR method of specimens heat treated at 350-600°C.

Correlation between DSC TTR and BFR A_f

The correlation between the DSC TTR and BFR A_f can be best demonstrated in Figure 5 which plots the DSC R_f' and A_f vs. the BFR A_f. It is clear that the DSC A_f which measures the finish temperature for the transformation from R-phase to austenite is generally higher than the BFR A_f while the R_f', the finish temperature for the transformation from martensite to R-phase, agrees very well with the BFR A_f.

Tensile Properties of Specimens with BFR A_f of 27+/-2°C

Tensile stress-strain curves of specimens having a BFR A_f in the range of 27+/-2°C are shown in Figures 6-9 and the key parameters are summarized in Table. 1. It is obvious from the data that

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