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A Study of the Properties of a Room Temperature Martensitic Binary Nitinol Alloy Above and Below its Martensite to Austenite Transformation Temperature

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Room temperature martensitic Nitinol alloys provide a challenge to end users of the material because they are martensitic and soft at room temperature. These are commonly referred to as Shape Memory alloys as they revert to their superelastic (pseudoelastic) form and austenitic structure at a temperature above ambient. For this study, a NiTi wire, Ti-55.3 wt.%Ni in composition (Alloy-B) and heat-treated to an Af ≈ 60 °C was used. Tensile testing was performed to fully characterize the performance of the material at a series of temperatures above and below its transformation temperature. This article will summarize the properties of the material along with the effects of multiple strains on key material performance characteristics.

Keywords austenitic, martensitic, nitinol, pseudoelastic, shape memory, strain, superelastic, tensile testing, transformation temperature

1. Introduction

As shown in previous studies, Nitinol alloys when fully recrystallized after high temperature annealing exhibit a single stage martensitic transformation from the parent B2 to B19′ monoclinic martensite. For functional use in a superelastic or shape memory application, the material is optimized by cold working and heat treating at lower temperatures so that nano-sized subgrains, a high density of dislocations, and very fine Ni-rich precipitates are present in the material (Ref 1, 2). This microstructure leads to a two-stage transformation of B2 → R Phase → B19′ martensite (Ref 1).

This study was developed to determine the effects of different heat treat temperatures and multiple strains on a NiTi wire, Ti-55.3 wt.%Ni in composition and heat-treated to an Af ≈ 60 °C. The first heat treat temperature used was at 525 °C for 4 min. This is a typical heat treat temperature and time that would be used for a Ti-55.8 wt.%Ni Nitinol to provide superelasticity at room temperature. The second lower heat treat temperature of 430 °C for 4 min was used to determine if the lower temperature would provide superior superelastic properties in the much warmer Ti-55.3 wt.%Ni alloy. The constant Af over a wide range of heat treatment parameters may be explained by the balancing effect between annealing and the precipitation of Ni-rich precipitates (Ref 1).

For the scope of this article, the ability of the Nitinol alloy to fully recover deformation strain is considered of primary importance. This deformation recovery is the functional property often used and specified by designers using shape memory alloys in their products.

2. Methods

2.1 Sample Preparation

Test samples were fabricated from a 40% cold worked ∅0.0428 wire (CW40-B-42.8). Samples for test were constrained on a fixture and shape set straight in a salt pot for the prescribed times and temperatures. This was followed by an immediate room temperature water quench.

2.2 Determination of Transformation Temperature

Transformation temperature was determined through both differential scanning calorimetry (DSC) per ASTM F2004 and bend and free recovery (BFR) per ASTM-F2082. Results from DSC and BFR agreed within one degree of each other. This is excellent correlation for alloys showing a clear R phase transformation (Ref 3). Only DSC data will be reported in this report.

2.3 Tensile Testing

Tensile testing was performed in a controlled temperature chamber using extensometer strain control per ASTM F2516.

3. Results

The data shown in Table 1 to 3 summarize the tensile testing performed at various temperatures on the straight

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Table 1 Typical room temperature martensitic heat treatment, Ti-55.3 wt.%Ni

	Heat treatment 525 °C/4 min, Af = 57 °C								
	Test temperature, °C								
	50	55	60	65	70	75	80	85	90
Stress at 3% strain 1st cycle, ksi	28	34	46	54	58	72	72	82	85
Residual strain 1st cycle, %	5.2	5.1	4.9	4.7	4.4	1.8	0.4	1.0	1.6
Stress at 3% strain 2nd cycle, ksi	106	103	100	89	77	62	69	69	73
Residual strain 2nd cycle, %	3.0	3.1	3.0	3.1	3.2	0.8	1.0	1.1	1.5
Stress at 3% strain 3rd cycle, ksi	167	155	165	161	155	54	66	60	76
Residual strain 3rd cycle , %	Break	Break	Break	Break	Break	1.4	1.0	1.6	1.2

Table 2 Modified room temperature martensitic heat treatment, Ti-55.3 wt.% Ni

	Heat treatment 430 °C/4 min Af = 58 °C					
	Test temperature, °C					
	50	55	60	65	70	75
Stress at 3% strain 1st cycle, ksi	55	59	68	71	78	81
Residual strain 1st cycle, %	4.0	0.3	0.1	0.1	0.1	0.1
Stress at 3% strain 2nd cycle, ksi	60	53	62	66	74	75
Residual strain 2nd cycle, %	3.2	3.7	0.0	0.0	0.1	0.1
Stress at 3% strain 3rd cycle, ksi	173	85	59	65	71	72
Residual strain 3rd cycle, %	Break	3.0	0.0	0.0	0.0	0.0

Table 3 Typical room temperature austenitic heat treatment, Ti-55.8 wt.%Ni

	Heat treatment 525 °C/4 min Af = 10 °C						
	Test temperature, °C						
	−20	−10	0	10	20	30	40
Stress at 3% strain 1st cycle, ksi	36	41	48	54	64	73	81
Residual strain 1st cycle, %	4.7	4.2	0.3	0.1	0.0	0.0	0.0
Stress at 3% strain 2nd cycle, ksi	40	39	46	52	61	69	77
Residual strain 2nd cycle, %	4.5	4.6	0.1	0.1	0.0	0.1	0.1
Stress at 3% strain 3rd cycle, ksi	33	36	45	51	61	70	75
Residual strain 3rd cycle, %	4.8	4.7	0.1	0.0	0.0	0.0	0.1

heat-treated wire samples. Each sample was pulled to 6% strain and then the load was reduced to less than 1 ksi. The cycle was repeated three times per sample at each temperature noted. The strain was balanced after each cycle (Fig. 1 to 6).

For comparison purposes, a room temperature superelastic alloy (Alloy-BB) was shape set using the high temperature (525 °C for 4 min) heat treatment. The same tensile testing was performed at temperatures both above and below its martensite to austenite transformation temperature. The results are tabulated in Table 1 to 3.

When subjected to a high temperature heat treatment typical of that used for a room temperature superelastic alloy, the warmer Alloy-B material did not develop its full superelastic properties until approximately 25 °C above its Af temperature. In contrast, the same alloy when heat treated at a lower temperature developed its full superelastic properties at its Af temperature. The room temperature superelastic material (Alloy-BB) actually developed its full superelastic properties 10 °C below its Af temperature. The above data and results are depicted in Fig. 7 to 12.

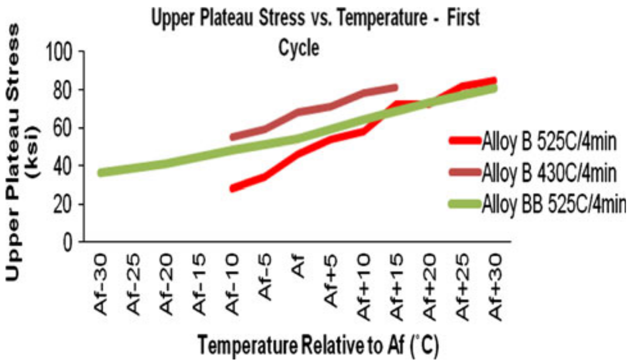

Fig. 1 Upper plateau stress vs. temperature—first cycle

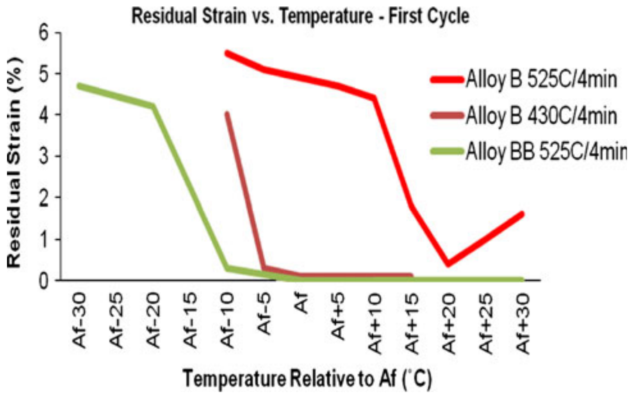

Fig. 2 Residual strain vs. temperature—first cycle

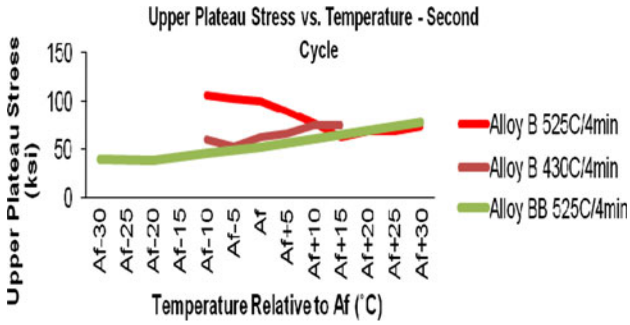

Fig. 3 Upper plateau stress vs. temperature—second cycle

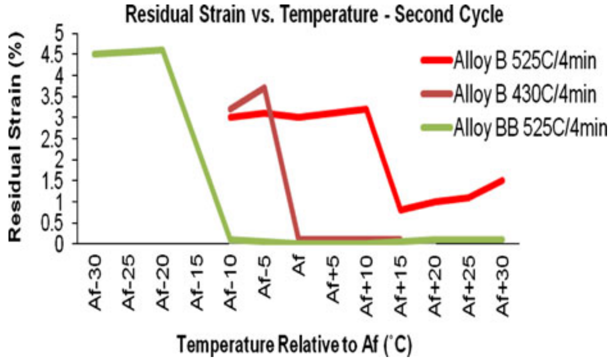

Fig. 4 Residual strain vs. temperature—second cycle

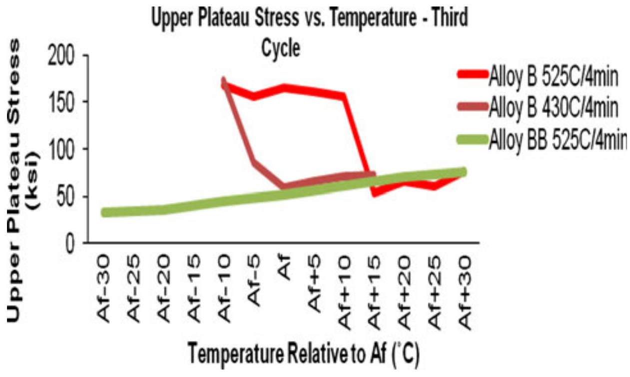

Fig. 5 Upper plateau stress vs. temperature—third cycle

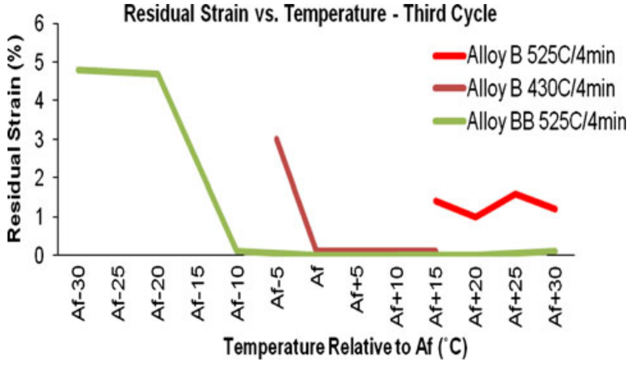

Fig. 6 Residual strain vs. temperature—third cycle

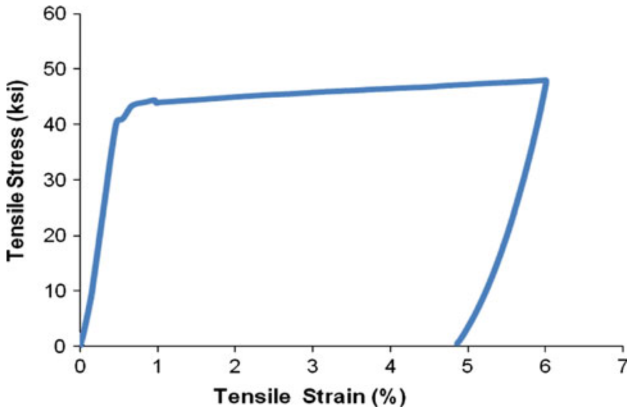

Fig. 7 Alloy B—heat treatment 525 °C/4 min tested at Af temperature

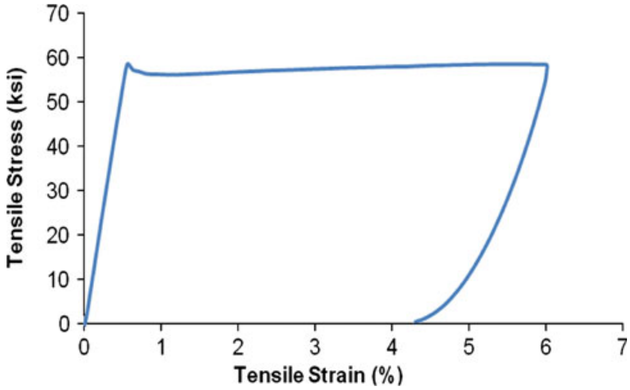

Fig. 8 Alloy B—heat treatment 525 °C/4 min tested at 10 °C above Af temperature

3.1 Tensile Test Graphs

Figures 7 to 12 are a graphical representations of the data presented above. Note the differences in superelastic plateaus depending on heat treatment and ambient temperature. The colder Alloy BB material shows much less dependence on ambient temperature than the warmer Alloy B material.

Figure 13 is a DSC scan representative of the typical results for a heat-treated sample used for this study. The graph clearly shows the two-stage transformation of B2 → R Phase → B19′ martensite (Ref 1).

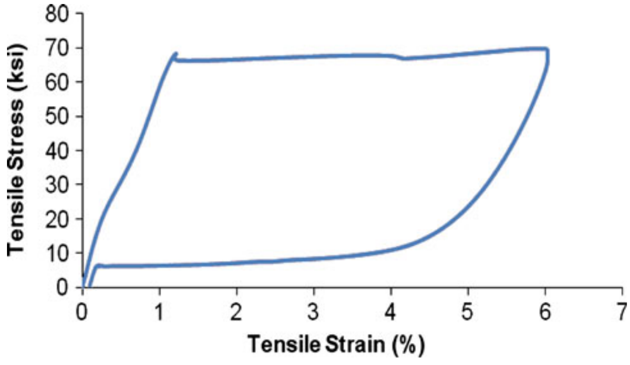

Fig. 9 Alloy B—heat treatment 430 °C/4 min tested at Af temperature

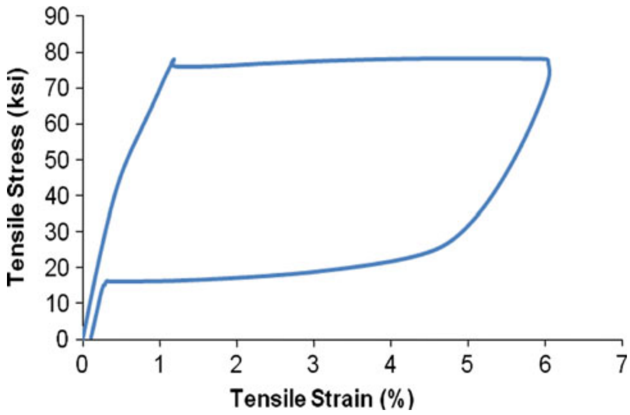

Fig. 10 Alloy B—heat treatment 430 °C/4 min tested at 10 °C above Af temperature

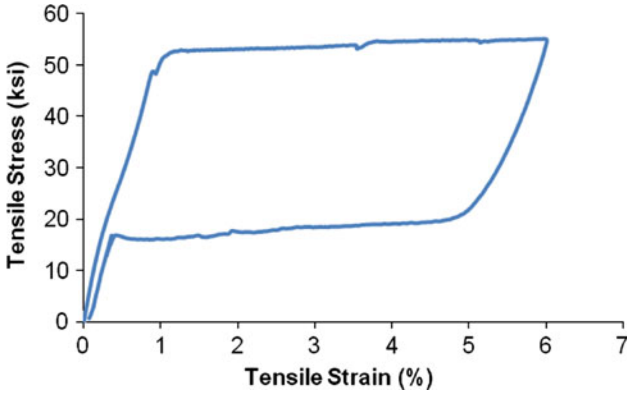

Fig. 11 Alloy BB—heat treatment 525 °C/4 min tested at Af temperature

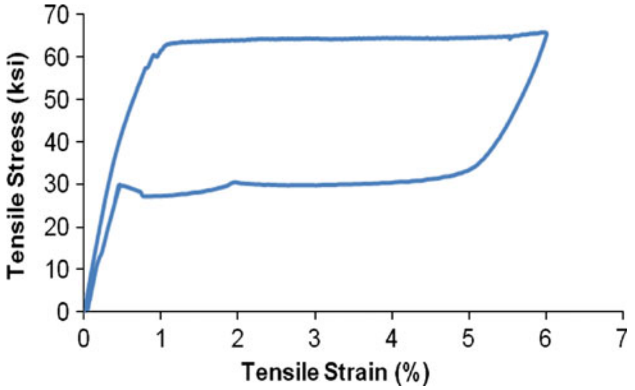

Fig. 12 Alloy BB—heat treatment 525 °C/4 min tested at 10 °C above Af temperature

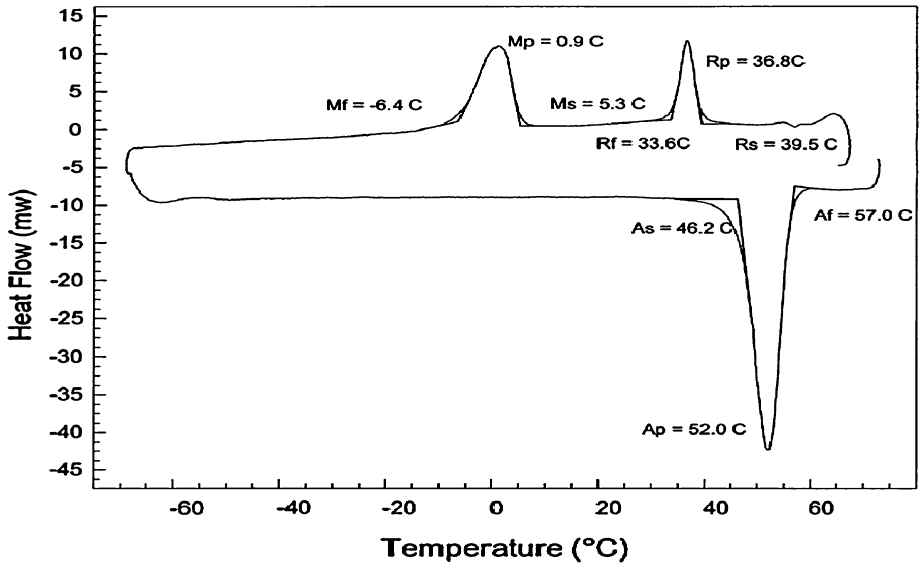

Fig. 13 DSC curve alloy B—heat treatment 525 °C/4 min

3.2 Fracture Surface Analysis

Scanning Electron Microscope (SEM) analysis was used to analyze the fracture surface on tensile test samples tested both above and below the sample martensite to austenite transformation temperature. Figure 14 to 17 depicts ductile yielding followed by overload fracture. The fracture surfaces exhibit

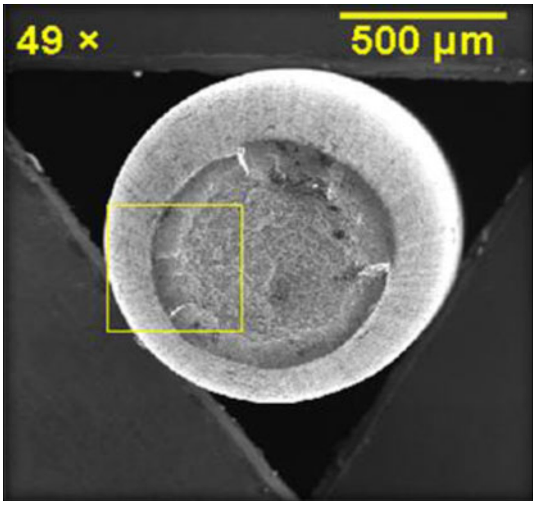

Fig. 14 SEM image of alloy B fracture surface at 20 °C

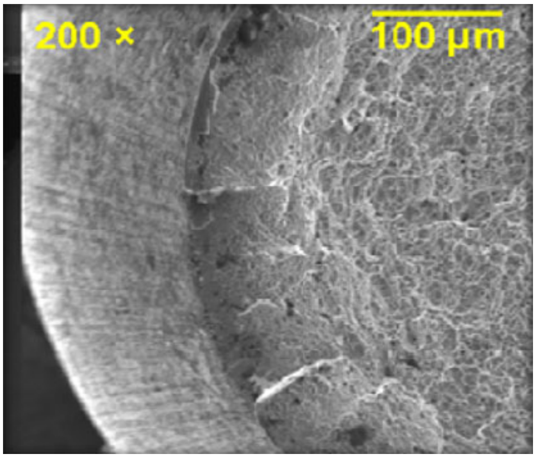

Fig. 15 SEM image of alloy B fracture surface at 20 °C

microvoid coalescence morphology independent of temperature or phase (Ref 4). This is consistent with previous research and literature.

4. Discussion and Conclusions

- The superelastic properties of a warm Ti-55.3 wt.%Ni alloy are much more dependent on heat treat temperature and ambient test temperature than a room temperature superelastic Ti-55.8 wt.%Ni alloy. This is due to the lower frequency of precipitates and dislocations in the lower Ni content alloy (Ref 2, 5).
- The higher heat treat temperature for the warmer Nitinol alloy also retards the nucleation and growth of the Ni-rich precipitates that act as barriers to dislocation motion and strengthen the alloy. This prevents the NiTi structure from providing full superelastic properties (Ref 2, 5). Further experiments on precipitate size and density by TEM may be required to confirm this theory.

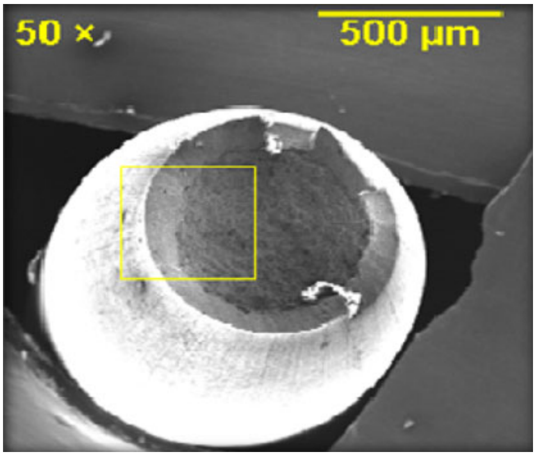

Fig. 16 SEM image of alloy B fracture surface at 75 °C

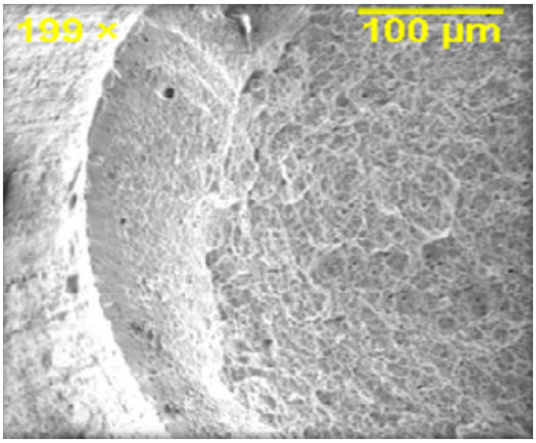

Fig. 17 SEM image of alloy B fracture surface at 75 °C

- The lower temperature heat treat for the Ti-55.3 wt.%Ni alloy provides superior superelastic properties to the higher temperature heat treat.
- The effect of the optimum heat treatment while evident on the initial strain cycle is exaggerated upon multiple strain cycles as seen in the accompanying data tables.
- As alloys are developed with different transformation temperatures, sufficient studies must be performed to determine the appropriate individual heat treatment. The times and temperatures needed to develop optimum properties are alloy dependent and cannot be carried over from prior experience.
- With the further development of ternary (NiTiCo for example) and other more complex alloys, this attention to alloy individuality will become more important.

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