An Investigation of Diverse Surface Finishes on Fatigue Properties of Superelastic Nitinol Wire

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Abstract

The impact of surface finish on rotary beam fatigue life of 0.323 mm Nitinol (Ni 56wt%-Ti) wire is studied. In preparation of the wire samples, processing parameters such as cold work reduction and annealing were held constant for all surface conditions investigated. Various Niti wire surfaces such as light oxide, dark oxide, black oxide, etched, pickled, mechanically polished, and electropolished are evaluated. These wires were subjected to alternating compression-tension cycles at strain levels ranging from 0.7% to 2.5% tested at ten degrees above the active A_f temperature. The choice of surface preparation directly affects the ultimate rotary beam fatigue life and becomes an important engineering design consideration necessary for the optimization of wire based implant medical devices.

Introduction

This paper studies the effect of zero mean strain rotary beam testing (RBT) of superelastic nitinol wires prepared with seven different surface conditions. When studying fatigue life three major considerations effect crack initiation and propagation leading to failure in nitinol wires: (a) melt chemistry, (b) processing and (c) surface condition. To isolate the effect of surface finish on fatigue life our study has taken care to prepare all samples from the same alloy heat, provide identical die reduction schedules, equal cold work amounts, and equivalent thermo-mechanical conditioning. Additional effort has been taken to provide a uniform ΔT between the specimen active A_f temperature and the RBT test temperature. It is our intent to provide useful fatigue information that can assist nitinol design engineers in selecting the appropriate surface condition to meet both the application fatigue requirements and optimal economic consideration.

Earlier strain controlled RBT studies were conducted by Kim, Y.S., et. al.[1] and Yang, J., et. al. [2] who demonstrated that fatigue life increased with decreasing test temperature at high level of strain (nitinol SIM range) and fatigue life is nearly independent of the test temperature in the lower strain amplitude ranges (nitinol elastic range).

A review of the RBT zero mean strain study by Reinoehl, et. al. investigated the effects of two different melt sources [3]. The research focused on 0.267 mm superelastic NiTi wires, processed with equivalent cold work reduction and annealing practice showed the RBT fatigue performance exhibited equivalent fatigue behavior regardless of statistically detectable differences in lower plateau stress, carbon level and inclusion content.

Patel, et. al. [4] studied the RBT fatigue effects of 0.323 mm Nitinol wires by varying the shape-setting temperature, creating a varying array of active A_f temperatures which later would be tested at a pair of test temperatures. This study experimentally shows that fatigue life would be dependent upon the temperature difference between the material active A_f and the test temperature.

Our study has followed the RBT test protocol developed by Patel [5].

A review of the literature cited above has not found any systematic studies that evaluate the RBT fatigue effects of varying the surface condition while keeping other variables constant. In addition, the authors cited above did not make reference to preparation of the wire surface condition. Our reasoning for this study is to eliminate as many variables as possible in the hope that a preferred surface preparation may become evident and lead to a better understanding of the surface condition effects on the RBT fatigue life.

Materials and Surface Processing

The current fatigue study focuses on 0.323 mm Nitinol (Ni 55.8 wt % - Ti Bal ; Ti 49.2 at %, Ni 50.8 at%) wire taken from the same section of VAR ingot. When measured by

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Differential Scanning Calorimetry, DSC, the ingot TTR (transformation temperature range) are as follows: A_s = -19.84°C; A_p = -11.84°C; A_f = -5.71°C. Nitinol round wires were cold worked from 2.16 mm to 0.323 mm with nominally 45% reduction in area, or cold work, on the final drawing die sequence.

The underlying base material was drawn utilizing single and multi crystalline diamond drawing die sequence technology. All cold worked wires were optimized to promote an exceptionally smooth and uniform surface finish. The process of preparing the cold worked surface condition consisted of various metal removal techniques (etching, pickling, mechanical polishing) and varying degrees of thermal oxidation.

Thermal Oxidation

The oxidation reaction of a nickel-titanium matrix was suggested by Zhu, et. al. [6] as following:

$$NiTi + O_2 \rightarrow Ni_3Ti + TiO_2 \rightarrow Ni_4Ti + TiO_2 \rightarrow Ni + TiO_2 \quad (1)$$

Hassel [7] further explains the diffusional effects of the metal cations and the oxygen anions associated with the production of an oxygen rich layer. It was stated that through thermally reacting O^{2-} with Ti^{4+} and Ni^{2+}, the surface structure and properties may be tailored to meet desired parameters

Pickling, Etching, Electropolishing

The process is coupled with a subsequent chemical treatment to further remove a slight amount of the base metal. The yielding surface is a rough surface texture. Hassel relates reactions at the Nitinol substrate through the basic chemical relationship [7]:

$$Me \rightarrow Me^{n+} + ne^{-} \quad (2)$$

A forward reaction prompts the metal to lose an electron though oxidation and the metal cation is solvated.
The following SEM images show six of the seven surface conditions used in this study prior to a final shape setting heat treatment.

Electropolishing follows the same general principle of Equation 2. In this case, the dissolution rate and conditions are controlled. The wire is anodically polarized in a solution that chemically dissolves the material. The potential and the dissolution rate are directly proportional [7].

Surface Conditions Used

Scanning electron microscopy photos are shown below for the six prepared cold worked surfaces used in this study.

The light oxide surface is shown in Fig. 1A and Fig. 1B, and captured at 200x and 2000x respectively. Visually these wires have a smooth, diamond drawn surface typically gold to brown in color.

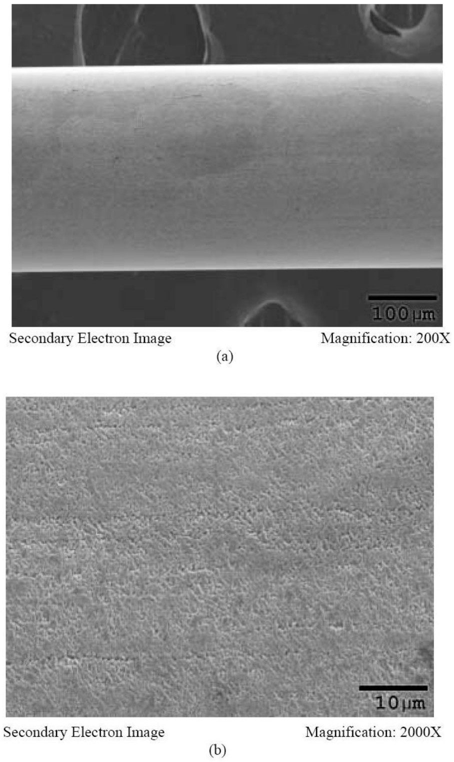

Figure 1A and 1B: Light oxide surface finish

The dark oxide appears as a gray to black color due to the introduction of a controlled oxygen-rich environment as portrayed in Fig. 2.

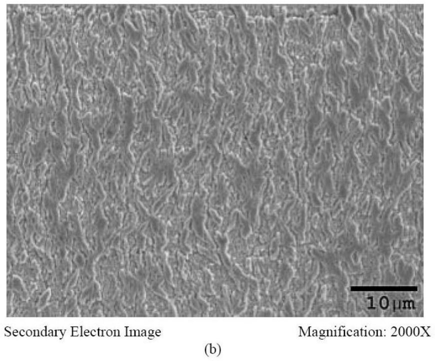

Figure 2: Dark oxide surface finish

Likewise, the denser black oxide, Fig. 3, exhibits a shiny black color, as a result of annealing in a modified oxidizing process as used in the dark oxide wire.

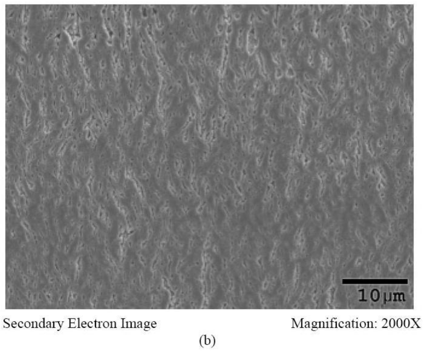

Figure 3: Black oxide surface finish

A chemical removal of the ceramic oxide layer creates an etched surface, essentially maintaining the level underlying diamond drawn surface unscathed, shown in Figure 4.

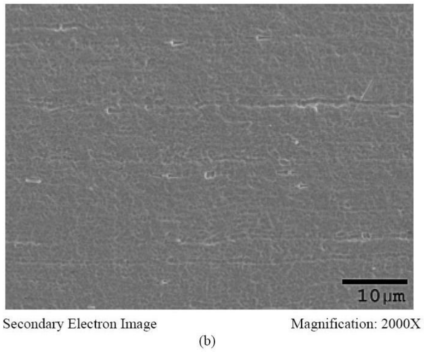

Figure 4: Etched surface finish

The surface in Figure 5 is pickled by exposure to a chemical agent to remove the oxide layer.

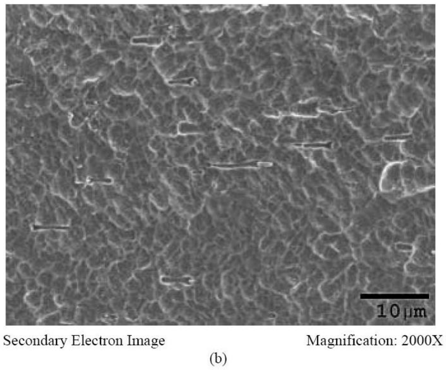

Figure 5: Pickled surface finish

To create the visually stainless steel-like appearance of the polished wire, a chemical removal of the oxide layer was followed by mechanical polishing. Scratches are evident at magnifications greater than 40x, as shown in Figure 6.

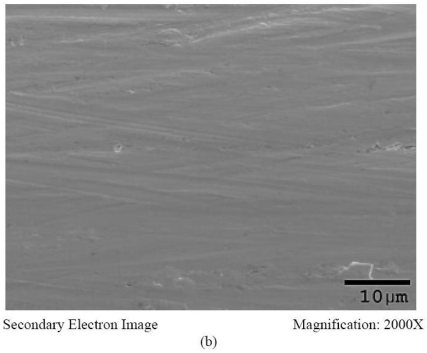

Figure 6: Mechanically polished surface finish

After preparation of the surface conditions shown, each nitinol wire is subjected to a shape-setting heat treatment. The shape setting process applied to these surface conditions is completed with the same oxidizing atmosphere, temperature, annealing time and tension.

The seventh wire studied was created from cold worked light oxide surface condition as shown in Fig. 1 by applying the shape setting treatment followed by electropolishing. This condition was chosen since it represent how material may be purchased from a wire supplier, shape set into a component and then electropolished (EP) to complete a finished medical device.

Experimental Test Method

The surface modification was the only variable adjusted in preparation for collecting the fatigue life data. The well documented dependence of stress and strain with temperature change in Nitinol materials obeys the Clausius-Clapeyron relationship [8]. To standardize the temperature dependence for all surface conditions the active A_f temperature was measured using the bend free recovery technique as defined by ASTM F2082. The purpose of this was to set the RBT and tensile test temperature at 10°C above the specimen active A_f to create a uniform ΔT. Table 1 gives the active A_f temperature for each of the surface conditions evaluated.

Table 1: Active A_f values of Niti Wires

Surface Finish	Active A_f (°C)	RBT Temp (°C)
Light Oxide	24	34
Dark Oxide	22	32
Black Oxide	24	34
Etched	18	28
Pickled	23	33
Mech. Polish	23	33
EP	23	33

A Positool Rotary Beam U-Bend Wire Spin Fatigue Tester (Model # 10-040) [9] was employed to evaluate the fatigue performance of the Niti round wires. Fatigue testing was completed in a temperature-controlled water bath. The following strain levels were tested: 0.70%, 0.80%, 0.90%, 1.00%, 1.50%, 2.00%, 2.50%. It was our goal to test seven samples for each surface condition at each of the strain levels. For each strain level, test completion was based on either wire fracture or by reaching a runout criterion of 100 million cycles. The material was cycled at a constant frequency of 3,600 revolutions per minute (RPM) [5].

Figure 7 shows the alternating strain amplitude (ε_a) versus fatigue life (N_f , the number of rotary beam alternating cycles) for all of the seven surface conditions. For each of the seven strain levels and seven surface conditions, there were approximately seven individual wires tested to failure to flush out a meaningful statistical average and identify any surface condition trends that effect fatigue life.

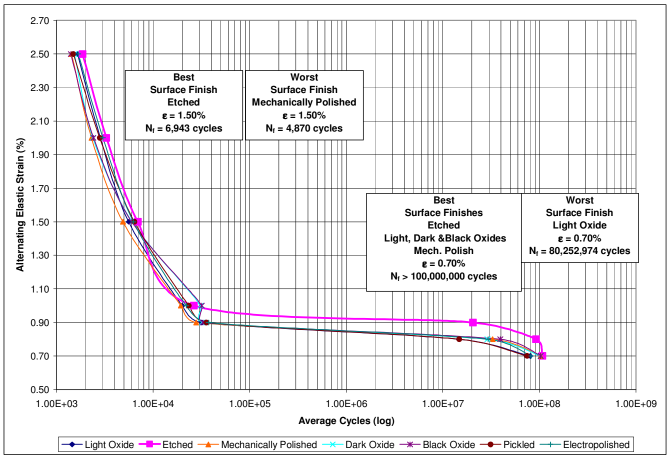

Figure 7: Alternating strain amplitude versus fatigue life for seven surface conditions

Results and Discussion

For purposes of discussion, it is convenient to break the fatigue life curve of Fig. 7 into three distinct regions. The first strain range begins at the knee of the curve and includes all strains < 0.9% where there is little or no stress induced martensite and the nitinol wires are operating below their proportional strain limit (ε_{pr} ~ 0.9%). The second strain range > 1.5% corresponds to a slight turning point in the fatigue life curve and corresponds to a region of stress induced martensite. Kim Y.S. [1] suggests the slight knee of the curve corresponds to the elastic limit of the material (ε_l ~ 1.5%). The third strain range covers everything in between 0.9% to 1.5% strain and is a region of the onset of stress induced martensite.

Strain Amplitude < 0.9%

Table 1 shows the total number of tested samples achieving 100 million cycles for strain levels less than the proportional strain limit. At 0.90% strain level no samples from any surface conditions survive the 100 million runout criteria. At 0.80% strain, more than twice as many etched wires survive to 100 million cycles when compared with the other prepared surface conditions. In addition, the average number of cycles to failure for the etched surface easily out performs the other surface condition for strain < 0.9%. The etched surface shown in Fig. 4 has one of the best surface appearances and many of the defects shown in the light oxide surface finish (Fig. 1) have been removed by the etching.

Table 2 : Total samples achieving 100 million cycles and the total # of samples tested

Surface Finish	Alternating Strain 0.90 %	 0.80 %	 0.70 %
Etched	1/5	6/7	7/7
Mech. Polish	0/7	3/7	7/7
Black Oxide	0/7	2/7	7/7
EP	0/7	2/7	4/5
Dark Oxide	0/7	1/7	7/7
Light Oxide	0/7	1/7	5/7
Pickled	0/7	1/7	5/7

Strain Amplitude Range > 0.9% and < 1.5%.

Figure 8 shows how the surface finishes compare at 1% strain amplitude. The black oxide, dark oxide and etched surface finishes all perform at the top end of the scale in terms of fatigue life. The mechanically polished surface finish performed poorly as might be expected.

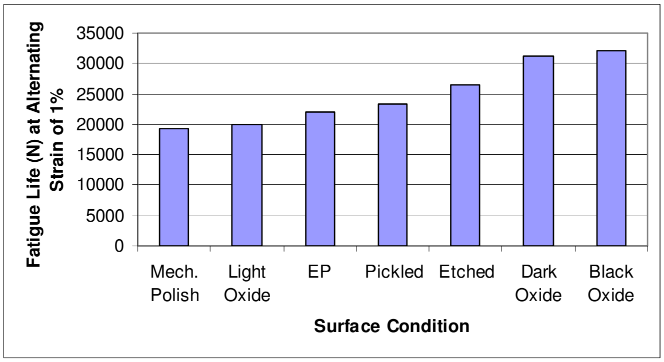

Figure 8: Fatigue life (N) versus surface condition at alternating strain of 1%

Strain Amplitude Range > 1.5%

Tensile test data was collected for all surface finishes prior to the first cycle. For the alternating strain range of 2.5%, surface finishes are arranged from highest to lowest loading plateau stress and the corresponding fatigue life was plotted as shown in Fig. 9. The etched specimen had the lowest plateau stress (before RBT) and the best fatigue life of all the surface conditions. The black oxide surface finish had the highest plateau stress (before RBT) and the worse fatigue life of all surface conditions. The fatigue life for highly strained wires operating in the stress-induced martensite range exhibits an inverse relationship to increasing plateau stress, see trend line below. The two exceptions are the aggressively pickled and the mechanically polished surface conditions as shown in Figs. 5 and 6, respectively. The increased surface roughness may be the cause for the premature fatigue life failure.

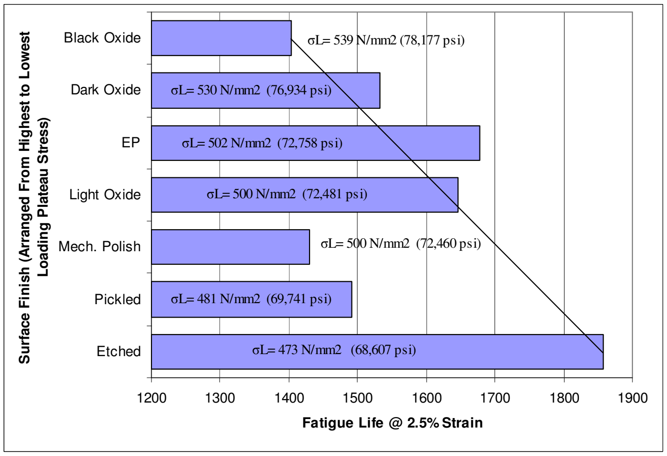

Figure 9: Plateau Stress Versus Fatigue Life at 2.5% Alternating Strain

Summary and Conclusion

1) Diamond drawn wires with varying surface finishes seem to weakly influence the fatigue life performance.

2) The etched surface out performs all other surface finishes for six of the seven alternating strains considered. This is especially evident in the elastic strain range < 0.9% where the fatigue limit has clearly been influence by this method of surface preparation. Etched surface specimens reached the runout condition at 0.9% and 0.8% strain at a greater frequency than other surface conditions studied. Additionally, it was noted the initial plateau stress was found to be the lowest of all surface finished studied however this should not influence the fatigue life when strains are less than 0.9% and no stress induced martensite is present.

3) In all total there were 339 rotating beam tests conducted at seven strain levels and for seven surface conditions. This evaluation represents the largest zero mean alternating strain fatigue study of its kind. This data has been combined and plotted as the average, minimum and maximum # of cycles to failure for each of the seven strain levels as shown in Fig. 10. The minimum fatigue limit observed from the study shows that a good safety margin is required especially when operating in the 0.7% alternating strain range. This combined fatigue curve should represent a valuable tool for nitinol design engineers.

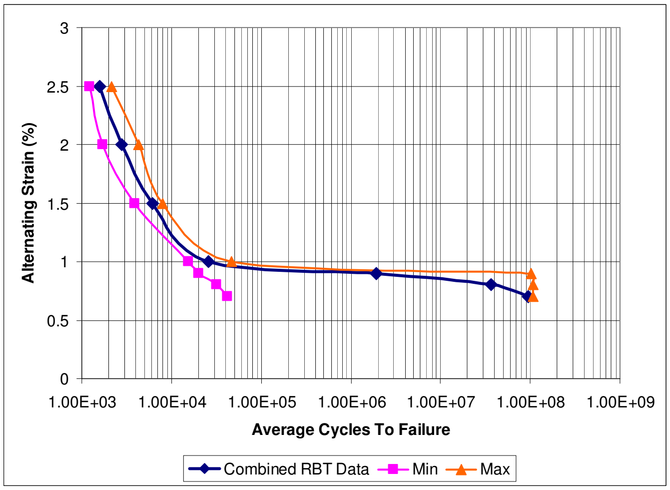

Figure 10: Average, Maximum and Minimum Results For All RBT Data

4) The scope of testing to complete this study prevented time for detailed fractography of the broken wires. A future study will examine the fractured wires, oxide composition,

thickness using surface imaging and EDS chemistry techniques to better understand the roll of surface interaction on fatigue life.

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