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HYDROGEN EFFECTS ON NITINOL FATIGUE

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ABSTRACT

This paper summarizes recent investigations of the influence of hydrogen on superelastic Nitinol (NiTi) and its effects on fatigue properties. ASTM Standard F-2063-00 limits hydrogen concentration to 50 wppm for wrought NiTi products (bar, wire, tube) used in the manufacture of medical devices and other surgical instruments. To date, however, no studies have linked this hydrogen standard to fatigue performance. The data presented here suggest hydrogen concentrations as low as 50 wppm cause a small yet statistically significant decrease in fatigue life above 1.4% cyclic strain. Increasing hydrogen concentration does not appear to affect fatigue life below 1.4% strain up to 80wppm hydrogen.

INTRODUCTION

Nitinol (NiTi) has many commercial applications including cell phone antennae wire, eyeglass frames, and orthodontic wire that take advantage of the unique engineering properties of the material. NiTi is also increasingly used in medical applications where fatigue performance is critical, such as in arterial stents, vena cava filters, and endodontic files [1]. Processing of finished Nitinol products are typically processed in hydrogen containing environments, including electropolishing, electroplating, chemical etching, and soldering [2]. It is clear from previous research that the mechanical properties of Nitinol in hydrogen containing environments differ from those in the absence of hydrogen [2-7]. It therefore follows that the effect of hydrogen must be considered when designing processing techniques and commercial applications for NiTi. Fatigue properties of hydrogen-containing NiTi medical devices are of particular interest because of the possible interaction between cyclic strain and hydrogen.

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Fatigue behaviour has also been studied extensively on both shape memory and superelastic NiTi [8-14]. Surprisingly, however, there is a dearth of published literature on the effects of hydrogen effects on fatigue behaviour. ASTM F-2063-00 specifies a limit of 50wppm hydrogen for wrought NiTi products (bar, wire, tube) used in the manufacture of medical devices [15]. Observations of hydride formation as low as 75 wppm H in austenitic and martensitic NiTi [6] provide motivation to explore the fatigue properties of NiTi with up to 100 wppm hydrogen. This paper therefore summarizes research on the influence of hydrogen on the fatigue properties of Nitinol.

MATERIALS AND METHODS

Electropolished NiTi wire with an A_f of 13°C and 0.8mm diameter with nominal 10 wppm H was hydrogenated at 80°C in 85% phosphoric acid for various times. Target hydrogen concentrations were 35, 50, and 80wppm. Multiple samples from each condition were analyzed by vacuum fusion hydrogen analysis at Luvak, Inc. (Boylston, MA).

Up to five samples each were fatigue tested at approximately 4.3%, 3.4%, 2.8%, and 2.0% half-amplitude alternating strain using custom built rotary bending equipment [16]. Up to 15 samples were tested at 1.4%, 0.7%, and 0.5% half amplitude alternating strain. Strain was estimated with $\varepsilon = r / \rho$ where ε is strain, r is the wire radius, and ρ is the radius of curvature. Each test was run in a room temperature water bath to a maximum of 10^7 cycles. Fracture surfaces were inspected with a JEOL JSM 5600 SEM in secondary electron image (SEI) mode at 20keV to 1000X.

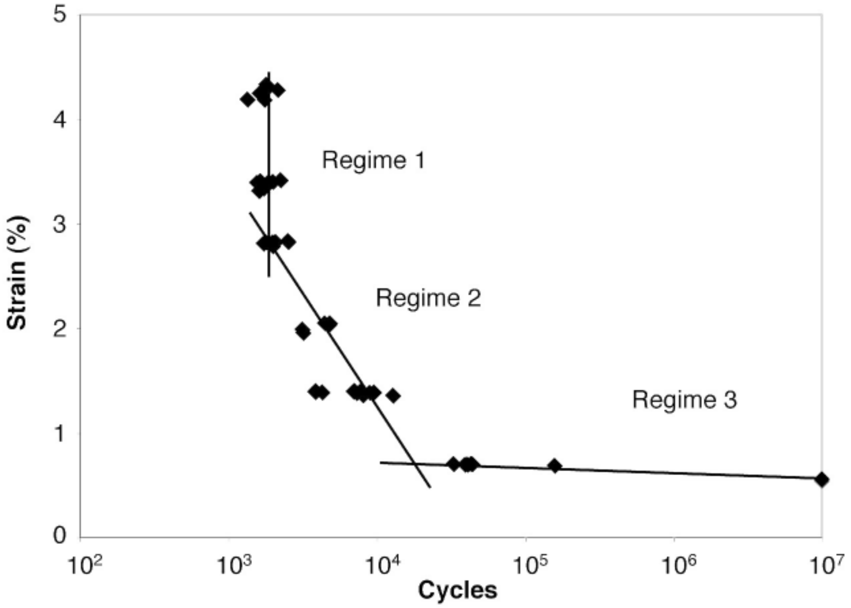

Fig. 1: Raw ε/N data from as-electropolished wires with 10 wppm hydrogen. Note the three distinct strain regions and the 0.7% endurance limit.

RESULTS AND DISCUSSION

Fig. 1 shows half-amplitude strain versus cycles to failure (ε/N) data for the 10wppm hydrogen wires. Note that multiple wires tested at 0.55% alternating strain were terminated without fracture at 10^7 cycles. The endurance limit, or the lowest value of strain that caused failure, was determined to be 0.7%. Overall, these 10wppm hydrogen fatigue data compare favourably to previous published rotary bend fatigue data, although no previous study explored the highest strain levels presented here [10-11]. Three trend lines can be fit to these data, which correspond to three distinct regimes of the ε/N curve labelled in Fig. 1. Regime 1 ($\leq 10^3$ cycles) extends from 4.5% to approximately 2.75% strain; Regime 2 represents strains from 2.75% to 0.75%. Regime 3 corresponds to high-cycle fatigue ($>10^4$ cycles).

Fig. 2 shows half-amplitude strain versus cycles to failure (ε/N) data for all wires tested during this study along with the trend lines from Fig. 1. It appears that the higher hydrogenated samples follow the same general trends as the electropolished wires. Furthermore, wires with each hydrogen concentration also reached 10^7 cycles at low strain levels without failure. Four important and general observations can be observed from these data:

1. The low-cycle fatigue data (Regime 1) are independent of strain on the order of 10^3 cycles.
2. Decreasing strain in Regime 2 leads to increasing fatigue life in the range of 10^3 to 10^5 cycles.
3. The average fatigue life in Regimes 1 and 2 tends to decrease with increasing hydrogen.
4. Higher cycle fatigue (Regime 3) is observed at the lower strains with larger deviations in the average cycle life.

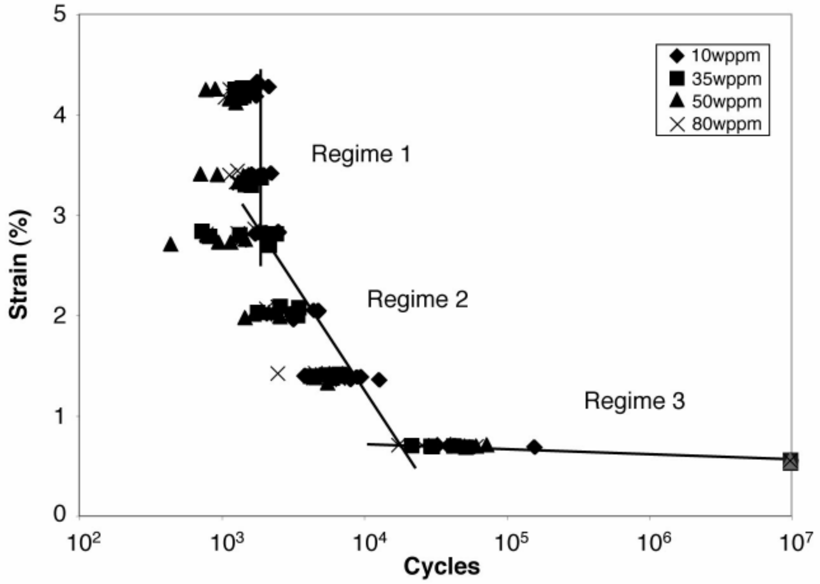

Fig. 2: ε/N data 10, 35, 50, and 80wppm H samples show similar trends with decreasing fatigue life with increasing hydrogen.

Fig. 3 illustrates representative SEM images from Regime 1 and Regime 2 for 10wwpm and 80wppm hydrogen. All samples showed crack initiation on the outer surface of the wire, subsequent crack propagation and then final failure. Furthermore, no systematic differences in the fracture initiation sites from each of the three regimes or with hydrogen content.

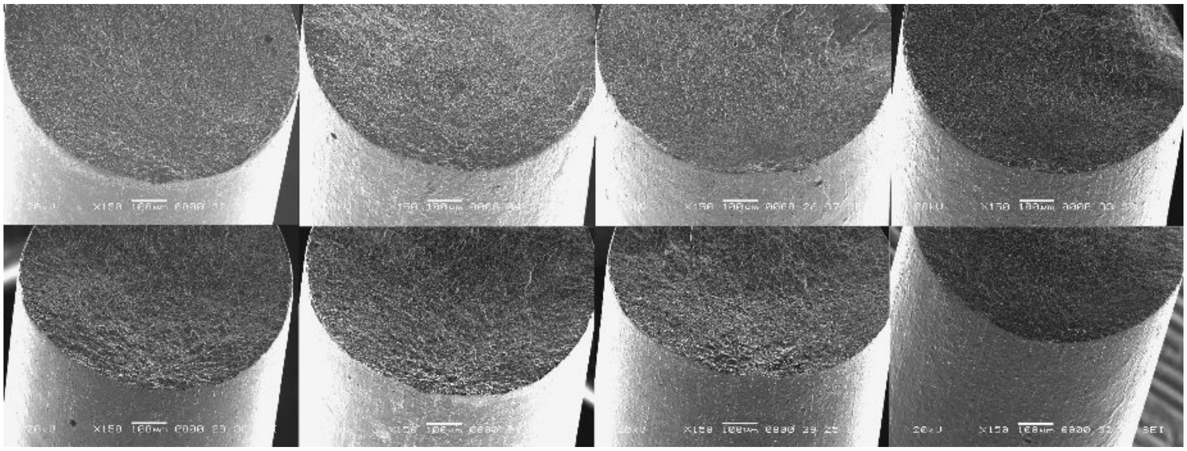
10 wppm 35 wppm 50 wppm 80 wppm

Fig. 3: Representative SEM images from 10- and 80 wwpm hydrogen levels at 3.4% (Regime 1) - top and 1.4% strain (Regime 2) - bottom. All images were taken in SEI mode, 20keV and 150X.

For rotary-bend fatigue testing, maximum tensile and compressive strain occurs in the wire outer fibres. During each revolution a single point on the wire surface alternates between maximum tension to maximum compression with a zero-mean strain. However, due to the well-known stress asymmetry between tension and compression [17] the mean strain may not be exactly zero. There is also a radial strain gradient in bending with zero strain at the neutral fibre.

In the present investigation, increasing hydrogen decreases average fatigue life above 1.40% strain with a pronounced effect above 2.75% strain. These strains roughly correspond to the transition from elastic deformation of austenite and stress-induced martensite for superelastic wire in pure bending conditions; there is a concomitant increase in volume fraction of martensite with increasing strain [18]. Miyazaki, *et al.* [10] proposed that the deformation modes influence the fatigue behaviour of superelastic NiTi during rotary bend testing.

The SEM images in Fig. 3 do not offer strong support for brittle fatigue fracture due to hydride formation as shown with monotonic fracture with larger hydrogen contents [2,4]. Nevertheless, the trend for decreased fatigue life in Regime 1 may result from the effects of interstitial hydrogen or tetragonal hydrides. If hydrogen is concentrated near the outer edge, the high hydrogen regions will superimpose with the high strain regions, thereby reducing the fatigue life. It is also important to recognize that the strains in Regime 1 correspond to the forward and reverse formation of stress-induced martensite. It has been shown that excessive amounts of hydrogen can decrease the thermal martensitic start transformation, which stabilizes austenite [2]. The results of Yamanaka, *et al.* [11] suggest that hydrogen may be more mobile in stress-induced martensite than in austenite, thus increasing the potential for high surface hydrogen to coincide with the stress-induced martensite regions. These investigators observed that hydrogen embrittled NiTi fractures more quickly when held at stresses above the critical martensite transformation stress compared to stresses below the critical martensite transformation stress. The authors also observed higher hydrogen absorption in the mixed stress-induced martensite and strained austenite than in stress-free austenite. It is expected that interstitial hydrogen will migrate preferentially to areas of highest strain states as observed in titanium alloys [19]. Under the conditions of rotary bend cyclic strain, it is likely that strain fields from hydrogen interact with the fatigue strains to reduce fatigue life.

In Regime 3, fatigue cycling occurs entirely in the elastic austenitic phase and there does not seem to be any differences in the fatigue behaviour with these hydrogen concentrations.

It is questionable whether it is appropriate to use a Coffin-Manson power-law analysis of NiTi fatigue behaviour [14], as first analyzed for NiTi by Melton and Mercier [8]. However, as observed by Wick, *et al*. [14], both test temperature and composition can influence the slope of fatigue life above about 1% alternating strain; these changes imply differences in cyclic strain accommodation. However, the present results indicate that there are no differences in the change in fatigue life with alternating strain for the 10-80 wppm hydrogen range. This observation indicates that there is not a mechanistic change with these low-levels of hydrogen.

Finally, a more limited study was conducted to investigate the fatigue influence of 100-200 wppm hydrogen. As will be reported in another publication, there is significant decrease in fatigue life (one-two orders of magnitude) in Regimes 1 and 2. Furthermore, there is a decrease in the fatigue strain at 10^7 cycles compared to samples with 10- to 80-wppm hydrogen.

CONCLUSIONS

This study investigated the effects of 10- to 80-wppm hydrogen on the fatigue behaviour of superelastic NiTi. The following observations were made:

- The data demonstrate a small but statistically significant trend of decreasing fatigue life with increasing hydrogen content. These effects were observed with as low as 50 wppm at or above 1.4% strain under low-cycle ($<10^4$), high strain ($>1.4\%$) fatigue conditions. This strain-cycle regime corresponds to the strain regions for stress-induced martensite in bending.
- Increasing hydrogen concentration does not appear to affect fatigue life below 1.4% strain up to 80wppm hydrogen. This is especially noteworthy since many medical devices are designed for service in this regime.
- Finally, there are no compelling data from the present investigation to indicate that stricter hydrogen limits should be considered for Nitinol devices.

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