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Sodium Hypochlorite Treatment and Nitinol Performance for Medical Devices

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Abstract

Processing of nitinol medical devices has evolved over the years as manufacturers have identified methods of reducing surface defects such as inclusions. One recent method proposes to soak nitinol medical devices in a 6% sodium hypochlorite (NaClO) solution as a means of identifying surface inclusions. Devices with surface inclusions could in theory then be removed from production because inclusions would interact with NaClO to form a visible black material on the nitinol surface. To understand the effects of an NaClO soak on performance, we compared as-received and NaClO-soaked nitinol wires with two different surface finishes (black oxide and electropolished). Pitting corrosion susceptibility was equivalent between the as-received and NaClO-soaked groups for both surface finishes. Nickel ion release increased in the NaClO-soaked group for black oxide nitinol, but was equivalent for electropolished nitinol. Fatigue testing revealed a lower fatigue life for NaClO-soaked black oxide nitinol at all alternating strains. With the exception of 0.83% alternating strain, NaClO-soaked and as-received electropolished nitinol had similar average fatigue life, but the NaClO-soaked group showed higher variability. NaClO-soaked electropolished nitinol had specimens with the lowest number of cycles to fracture for all alternating strains tested with the exception of the highest alternating strain 1.2%. The NaClO treatment identified only one specimen with surface inclusions and caused readily identifiable

surface damage to the black oxide nitinol. Damage from the NaClO soak to electropolished nitinol surface also appears to have occurred and is likely the cause of the increased variability of the fatigue results. Overall, the NaClO soak appears to not lead to an improvement in nitinol performance and seems to be damaging to the nitinol surface in ways that may not be detectable with a simple visual inspection for black material on the nitinol surface.

Keywords

corrosion; fatigue; nickel ion release; nitinol; sodium hypochlorite; surface inclusions

1. Introduction

Because of its unique material properties, nitinol has become a popular material for medical devices. Today nitinol is used in devices including transcatheter heart valves, vascular stents, endovascular grafts, endodontic files, inferior vena cava filters, atrial septal defect occluders, and bone staples (Ref 1–3). As experience with nitinol has increased over the years, so has the medical device community's understanding of the importance of processing and microstructure on nitinol performance such as corrosion susceptibility, nickel release, and fatigue resistance (Ref 4, 5). During the nitinol manufacturing process, inclusions are formed as small quantities of oxygen and carbon are introduced into the material. Inclusions are present throughout the material and can be of concern in medical devices as they tend to be associated with fatigue crack initiation (Ref 1). Inclusions may also be linked to pitting corrosion, although there has not been consensus on this point to date (Ref 6, 7). Recognizing the importance of controlling inclusions such as $\text{Ti}_4\text{Ni}_2\text{O}_x$ and TiC , the industry standard for nitinol alloys used in medical devices and surgical implants, ASTM F2063, places an upper limit on inclusion size of $39.0\text{ }\mu\text{m}$ (Ref 8). Inclusions are an important research topic, and recent experimental and modeling efforts have been making progress toward better understanding how inclusions affect fatigue life (Ref 9–11). In one recent study, Robertson et al. (Ref 10) examined the role of inclusions in fatigue by comparing the fatigue life of three standard nitinol production methods with that of two newer methods designed to reduce the size and/or number of inclusions and found that the newer process resulted in approximately a twofold increase in the strain limit at 10 million cycles. Because of the negative impact that inclusions can have on nitinol performance, there is a great deal of interest in reducing the number of inclusions and in reducing their size in finished medical devices.

Current industry practice regarding inclusions in nitinol relies on ASTM F2063 for defining an acceptable size limit and on visual methods such as ASTM E1245 (Ref 12) for detecting inclusions. Recently, a new method has been proposed to simultaneously sterilize and screen nitinol medical devices so that devices with surface inclusions could be readily identified (Ref 13, 14). In this method, nitinol devices are subjected to a soak in 6% sodium hypochlorite (NaClO), commonly known as liquid bleach, for 15 min at room temperature followed by a rinse in distilled water. Under this paradigm, it is suggested that devices with surface inclusions will begin to produce a black flocculent material that is easily identifiable via visual inspection during the NaClO soak as nickel from nickel containing inclusions or

from nickel-rich regions near non-nickel containing inclusions reacts with NaClO. Those devices that show visual evidence of a black flocculent material could then be removed from production, while others that do not could continue in production because they would have been identified as free of surface inclusions. However, there are concerns related to this method as previous research has shown damage to nitinol surfaces after soaking in NaClO solutions (Ref 15). Therefore, in order to better understand how an NaClO soak might affect medical device performance, we compared as-received and NaClO-soaked nitinol wire specimens in terms of corrosion, nickel release, and fatigue performance.

2. Materials and Methods

2.1 Materials and Sodium Hypochlorite (NaClO) Treatment

Superelastic nitinol wires with two different surface finishes were selected for this study: black oxide (BO) and electropolished (EP). These surface finishes were selected to encompass a range of potential surface qualities in implantable nitinol devices (Ref 5, 16). The electropolishing procedure was standard in nature, i.e., no ultrasound, magnetic fields, or other special techniques were applied during the procedure. Surface analysis using Auger electron spectroscopy was conducted by Evans Analytical Group (Sunnyvale, CA) at one spot on each material. The oxide thicknesses were determined based on the full-width-at-half-maximum method to be 651 nm for the BO nitinol and 11 nm for the EP nitinol; the accompanying depth profiles are shown in Fig. 1. Wires of 0.5 mm diameter were selected for all the testing because they are simple to manipulate for our tests, easy to obtain, and a good representation of medical devices in terms of their size and geometry. All the materials used conformed to ASTM F2063.

Prior to performance testing, specimens were split into two groups and subjected to either nothing (i.e., as received) or a 6% NaClO (Fisher Scientific) soak for 15 min followed by a deionized water rinse. Cut wire ends were coated with a small amount of lacquer before the NaClO soak to ensure that no bulk material was exposed to NaClO. As-received wires were not rinsed in deionized water.

2.2 Pitting Corrosion Susceptibility

Pitting corrosion susceptibility was evaluated by cyclic potentiodynamic polarization testing per ASTM F2129 (Ref 17). Six samples of each surface finish and condition (NaClO soak and as received) were tested using a Gamry Interface 1000 potentiostat (Warminster, PA). Briefly, specimens were placed into a deaerated phosphate-buffered saline (PBS) solution (Fisher Scientific) at 37 °C and allowed to equilibrate for 60 min while the open-circuit potential was recorded. After the equilibration period, the potential was increased to 1000 mV at 1 mV/s and then reversed while the current was monitored. Rest potential (E_r) was recorded at the end of the equilibration period and breakdown potential (E_b), if breakdown occurred, was recorded as the potential when a greater than two decade increase in current was observed with pitting corrosion confirmed by visual inspection. Over potential ($E_b - E_r$), defined as the difference between breakdown and rest potential, was also calculated and recorded. Statistical comparisons between NaClO-soaked and as-received groups were made with either two-sample t-tests or log-rank analysis. Log-rank analysis was used only with

right-censored data sets (i.e., when no breakdown occurred and E_b was recorded as 1000 mV).

2.3 Nickel Ion Release

As-received and NaClO-soaked BO and EP nitinol wires ($n = 6/\text{group}$) were immersed in PBS at 37 °C for 14 days. Nickel release testing followed previously published methods (Ref 5). Each wire (32 mm exposed length) was placed into a polypropylene container and filled with 4 mL of PBS resulting in a wire surface area to PBS volume ratio of 0.13 cm²/mL. All containers used for immersion of wires were acid-washed using a 10% HNO₃ solution (A509-P212, Fisher Scientific, Pittsburgh, PA) prior to use. At Days 1, 2, 7, and 14, each wire was removed from its container and placed into a new container of fresh PBS. A 4% HNO₃ solution (Optima A467-P500, Fisher Scientific, Pittsburgh, PA) was added to all completed PBS samples to ensure that any precipitated nickel would dissolve back into solution.

PBS solutions were analyzed for nickel using an Agilent 7500ce inductively coupled plasma mass spectrometer (Agilent Technologies, USA) fitted with an octopole collision/reaction cell pressurized with helium (UHP grade). Sample introduction and instrument tuning parameters were optimized for the nickel-60 isotope. Scandium-45 was used as an internal quantification standard. Calibration standards were prepared using Ni and Sc stock solutions obtained from high-purity standards (1036-1 and 100048-1, respectively). EP nitinol wire PBS solutions were diluted at a ratio of 1:5, and BO nitinol wire PBS solutions were diluted at a ratio of 1:100. Samples with values above the highest calibration point were diluted further. Four-point calibration curves were used to analyze the PBS solutions. The slopes for all calibration curves had correlation coefficients greater than 0.9995, and the calibrations were verified using NIST SRM 1640a, Trace Metals in Water. Check standards and reagent blanks were analyzed throughout the study, and no significant deterioration of the detection limit or calibration drift was observed. Nickel recovery was verified with spike tests ($n = 4$) that resulted in a 93-94% recovery. In addition, duplicate samples were randomly analyzed to verify analyte recovery method repeatability (<1 ppb difference for EP nitinol wire PBS solutions and <5 ppb difference for BO nitinol wire PBS solutions). PBS blanks ($n = 6$) possessed Ni values below 1 ppb; therefore, limit of quantification was approximately 1 ppb. Analysis of variance (ANOVA) with Tukey's pairwise comparisons was used to assess differences between NaClO-soaked and as-received groups for EP and BO nitinol wires at each time point. P values less than 0.05 were considered significant.

2.4 Fatigue

Rotary bend wire fatigue testing was conducted at 60 Hz in PBS at 37 °C using Valley Instruments (Brunswick, OH) or Blockwise Engineering (Tempe, AZ) wire fatigue testers in a guided bend test configuration per ASTM E2948 (Ref 18). Alternating strains varied from 0.56 to 1.20% for BO nitinol and from 0.69 to 1.20% for EP nitinol. Tests were conducted until fracture or run out at 100 million cycles. Six specimens from each surface finish and condition were tested at each alternating strain level. Statistical comparisons between NaClO-soaked and as-received specimens for each nitinol surface finish and alternating strain were made using either Welch's t test or log-rank analyses with $p < 0.05$ considered

significant. Log-rank analyses were used for the lowest alternating strain data sets because of the right-censored data (run outs at 100,000,000 cycles), and Welch's t test was used in place of a standard t test because of unequal variances between groups. To quantify differences in variability, coefficient of variation was calculated as the standard deviation divided by the mean at each alternating strain and for each condition.

2.5 Scanning Electron Microscopy

A JEOL JSM-6390 (Peabody, MA) scanning electron microscope (SEM) was used to image specimens in the as-received and NaClO-soaked states. Wire specimens were rinsed with 70% isopropanol and air-dried before they were mounted onto specimen holders using a double-sided carbon conductive tape (Ted Pella Inc, Redding, CA). SEM micrographs of fracture surfaces and sides of wire specimens were acquired using secondary and backscatter modes. The secondary imaging mode was used to observe the morphology of the specimen surface, while the backscatter mode was used to distinguish inclusions, pits, and surface defects on the imaged surface. Energy-dispersive spectroscopy (EDS) (NORAN System Six, Thermo Scientific, Waltham, MA) was used to determine whether features appearing dark on the backscatter images were inclusions on the surface of the wires based on their elemental composition.

3. Results

3.1 Sodium Hypochlorite Treatment

NaClO soaking of EP and BO nitinol was completed to generate a total of 72 soaked specimens for the fatigue, corrosion, and nickel release testing. After the NaClO soak, visible black flocculent was not present on any of the EP nitinol specimens, but a small amount was observed on one of the BO nitinol specimens intended for fatigue testing as shown in Fig. 2. The specimen with black flocculent material was discarded and an additional BO nitinol specimen was soaked in NaClO as a replacement. SEM micrographs of BO and EP nitinol wires before and after NaClO soaking are shown in Fig. 3. All the wires imaged by SEM after NaClO soak had passed the visual test for black flocculent. Corrosion pits were observed on the BO nitinol after NaClO soaking but not on the EP nitinol. Figure 4 shows SEM micrographs of surface inclusions on as-received and NaClO-soaked EP nitinol wire specimens with corresponding EDS spectrum of the inclusion taken after fatigue testing was completed. Both inclusions have a similar appearance and have spectra with similar peaks, indicating that the NaClO solution did not react with the inclusion on the NaClO-soaked sample or identify it.

3.2 Pitting Corrosion Susceptibility

Results of the pitting corrosion susceptibility are given in Table 1 and Fig. 5. In general, while there were major differences in the corrosion behavior between the BO and EP nitinol, there were only minor differences between the NaClO-soaked and as-received groups for both materials. The representative potentiodynamic curves in Fig. 5 illustrate the similarities between the as-received and NaClO-soaked groups for both BO and EP nitinol. All of the BO nitinol wires experienced breakdown, while none of the EP nitinol wires experienced breakdown. There were no statistical differences in breakdown potential between as received

and NaClO soaked for either EP or BO nitinol. After NaClO soaking, rest potential decreased slightly for the BO nitinol and increased slightly for EP nitinol. Although relatively small for both nitinol surface finishes, the difference in rest potential between as received and NaClO soaked reached statistical significance for BO nitinol, but not for EP nitinol. NaClO soaking led to a statistically significant increase in over potential for BO nitinol and a statistically significant decrease for EP nitinol.

3.3 Nickel Ion Release

Ni release results are shown in Fig. 6. For EP nitinol wires, NaClO soaking resulted in similar nickel release compared to as-received wires for all time points ($p > 0.99$). For BO nitinol wires at Day 1, NaClO soaking resulted in significantly increased nickel release compared to as-received wires ($p = 0.002$). However, nickel release was similar between NaClO-soaked and as-received wires for Days 2, 7, and 14 ($p > 0.70$). EP nitinol wires released significantly less nickel compared to BO nitinol wires for all time points and soak conditions ($p < 0.001$).

3.4 Fatigue

Fatigue test results are given in Tables 2, 3, 4, and 5 as well as in Fig. 7. On average for BO nitinol, the NaClO-soaked wires were observed to fracture sooner than the as-received wires at all strain levels tested; statistically significant differences ($p < 0.05$) were observed at 1.2 and 0.8% strain. EP nitinol showed a similar average number of cycles to fracture for both groups with the NaClO-soaked group having an increased number of cycles to fracture at an alternating strain of 0.83%; statistically significant differences were not observed at any alternating strain. In general, the NaClO soak resulted in data with higher variability for both surface finishes. When directly comparing strain levels for each nitinol, the coefficient of variation and range (maximum – minimum number of cycles) were higher in the NaClO-soaked group than in the as-received group for seven out of eight comparisons. Similarly, directly comparing the NaClO-soaked and as-received groups for each nitinol surface finish and strain level, the NaClO-soaked group contained the specimen with the lowest number of cycles to fracture seven out of eight times. Figure 8 shows SEM micrographs of fracture surfaces from as-received and NaClO-soaked groups for both nitinol surface finishes. The specimen chosen for imaging from each group was the one with the smallest number of cycles to fracture. Both EP nitinol specimens and the as-received BO nitinol image have visible inclusions near the fatigue crack initiation site. The NaClO-soaked BO nitinol wire, however, has what appears to be a corrosion pit at the fatigue crack initiation site.

4. Discussion

In the course of preparing 72 NaClO-soaked specimens, only one of the BO nitinol wires was found to have a black flocculent material on its surface after 15 min of soaking. However, as shown in Fig. 4 and 8, some surface inclusions were not identified by the screening procedure which casts doubt on the method's effectiveness. Additionally, as a detection method it seems plausible that operators conducting such a screen could overlook the black flocculent material given its small size relative to a typical stent strut (Fig. 2) and inadvertently send a damaged part further down the production line. The NaClO soak was

found to be capable of causing corrosion damage to the nitinol surface even when no black flocculent material was observed during the soak as shown in Fig. 3. This type of corrosion damage was likely the site of the early fatigue fracture documented in the NaClO-soaked BO nitinol sample shown in Fig. 8 and may explain why the NaClO-soaked group underperformed the as-received group at every alternating strain level for BO nitinol. Interestingly, the corrosion damage shown in Fig. 8 bears a strong resemblance to images from an unrelated study in our laboratory where corrosion damage was electrochemically induced during fatigue and similarly led to a reduced fatigue life (Ref 19). Here, as in the other study, corrosion pits were identified to be the site of initiation for a fatigue crack. The main difference between the present work and the referenced study is that the corrosion damage here was likely caused during the NaClO soak, while in the other study the corrosion damage was induced during cyclic fatigue. This kind of readily observable damage was limited to the BO nitinol, whereas the NaClO soak appeared to have a more subtle effect on the EP nitinol. With the exception of 1.2% alternating strain, the NaClO soak led to both the highest and lowest number of cycles to fracture, i.e., the largest range of fatigue life, for all the EP nitinol fatigue tests. Although we were unable to identify differences at the crack initiation sites between as-received and NaClO-soaked fatigue specimens, the results appear to suggest that the NaClO soak can have either a positive or negative effect on the fatigue life of an individual specimen. In total, however, the results point to the NaClO soak causing a higher variability in fatigue life which would be undesirable for a manufacturer looking to increase fatigue life. Although one might expect to see an improvement in performance for the NaClO-soaked group because specimens with surface inclusions that could act as fatigue crack initiation sites would be removed from testing, this was not the case in our study and no improvement was observed for the NaClO-soaked group.

In our tests, nickel ion release was mostly unaffected by the NaClO soak with the exception of BO nitinol showing higher nickel release at Day 1. We suspect that corrosion damage from the NaClO soak resulted in a higher bolus of nickel leaching upon initial immersion, but did not persist once repassivation of the oxide layer occurred. Since corrosion damage was not observed in NaClO-soaked EP nitinol, it was expected that no differences in nickel ion release would be observed over the two-week test. Regardless of the NaClO soak, we found that BO nitinol released more nickel than EP nitinol which agrees with previous work on laser-cut nitinol stents (Ref 5). Because nitinol performance is dependent on processing, it is difficult to speculate how a chemically etched surface or a different electropolish would respond to an NaClO soak in terms of nickel release. For our tests, we chose the BO and EP nitinol to attempt to bookend expected performance by having drastically different oxide thicknesses (11 nm for EP nitinol and 651 nm for BO nitinol). These oxide thicknesses are within the range of other studies on nitinol wires and stents (Ref 5, 16, 20, 21). Presumably other nitinol surface finishes would have similar or at least not worse performance after an NaClO soak. However, because of the difficulty in predicting possible effects from an NaClO soak on other surface finishes, further testing would be warranted to see how material performance is affected for a particular nitinol surface finish. Corrosion susceptibility as measured by ASTM F2129 was generally unaffected by the NaClO soak in our tests. Regardless of NaClO condition, EP nitinol had higher breakdown potentials than BO nitinol similar to other studies (Ref 16, 22). The NaClO soak led to a statistically

significant decrease in rest potential for the BO nitinol although the absolute change in average E_r was within the range of expected variability for the test as described in ASTM F2129. The EP nitinol that underwent the NaClO soak had a slightly increased rest potential compared to the as-received group, but again the change was within expected variation for this test. Most importantly regarding the corrosion susceptibility, no statistically significant change in breakdown potential was observed for either nitinol surface finish after the NaClO soak. A reduction in breakdown potential after NaClO soaking might have been expected for BO nitinol given the corrosive damage observed in Fig. 3. One potential explanation for the lack of difference is that the BO nitinol had such a low E_b in the as-received state that any corrosion pits caused by the NaClO soak were not able to reduce the E_b further. It is unclear how the NaClO soak might affect nitinol with an intermediate surface finish quality in terms of breakdown potential and further testing would be warranted given the ability of the NaClO soak to cause corrosive damage to the BO nitinol. With respect to over potential, we observed a statistically significant increase after NaClO soak for BO nitinol and a statistically significant decrease for EP nitinol. Similar to the rest potential data though, the absolute differences between mean values are within expected variability for this test so while the results were statistically significant, they do not provide strong evidence for a change in corrosion susceptibility after NaClO soaking. The over potential values for EP nitinol, in particular, should be interpreted with caution because no breakdown was observed for any EP nitinol sample. Given the censored breakdown potential data, the statistical significance for this comparison arises from the difference in rest potential alone and is probably not a reflection of a change to the corrosion susceptibility of EP nitinol in response to the NaClO soak. In comparison with the fatigue tests, the corrosion and nickel release tests appeared to not be as sensitive to the type of changes that the NaClO soak caused to nitinol.

Because of the use of NaClO as an irrigant during root canal procedures and as a disinfectant, relevant research has been done on the effects of NaClO soaking on the fatigue resistance of nitinol endodontic instruments. Although the results may not be directly comparable to the present work because of differences in the numbers of cycles to fracture, NaClO concentration, and temperature of the NaClO soak, it is nevertheless informative to review the similarities and differences of this testing. In two separate papers, Berutti et al. (Ref 23) and Peters et al. (Ref 24) investigated the effects of a 5 or 5.25% NaClO solution soak, respectively, under elevated temperatures at times that varied from 5 min to 2 h and found reductions in nitinol fatigue life. Both authors, however, point out that the reductions in fatigue life may have been caused by galvanic corrosion between nitinol and another metallic component of the instrument during the NaClO soak. Although there was no other metal present in our study to create a galvanic couple, many nitinol devices have radiopaque markers that could allow for galvanic corrosion during an NaClO soak and lead to damaging corrosion of the nitinol frame; this aspect of the NaClO soak method would require careful consideration before any implementation as part of a device production process. Martins et al. (Ref 25) studied the effect of a 24-h 5.25% NaClO soak of only the nitinol portion of an endodontic instrument and found that the soak did not have any effect on fatigue life as compared to a non-soaked control. However, the number of cycles to fracture was <1000 which is substantially lower than our experiments and may not be directly comparable.

Similarly, Pedulla et al. (Ref 26) compared the effects of 1- or 5-min static or dynamic 5% NaClO soak at 37 °C and found no change in fatigue behavior. In contrast, Topcuoglu et al. (Ref 27) observed a reduction in fatigue life for one of three endodontic files tested after a dynamic immersion in 5% NaClO at 37 °C for 5 min, but not for the other two files. It is unclear whether the differences observed in fatigue life among those three endodontic files were a result of nitinol material differences or design differences, but the results from our study here suggest that it is possible that the differences in fatigue life among endodontic files after NaClO soaking observed by Topcuoglu et al. could have been related to differences in nitinol surface finish.

One other area where NaClO treatment has previously been used in conjunction with nitinol is in the decontamination of explanted medical devices prior to their analysis (Ref 28). Following the use of NaClO for decontamination of explants, Lasley et al. (Ref 15) studied different decontamination solutions to determine whether the solutions themselves were capable of causing artifactual corrosion in nitinol. Similar to our study, Lasley et al. studied nitinol wires with different surface finishes. Using 6 and 1.2% NaClO, they conducted soaks for 2 h or more and then examined the wire surfaces using SEM and EDS methods. After 2 h, the 6% NaClO soak resulted in differing levels of corrosion in all three nitinol surface finishes, whereas the 1.2% NaClO soak resulted in corrosion of only two of the nitinol surface finishes. The third nitinol surface finish did show signs of corrosion, but not until 3 days of exposure to 1.2% NaClO. Similar to our study, the authors found the response to NaClO to vary depending on the nitinol surface finish. Interestingly, there also appeared to be a time effect with longer soak times resulting in more corrosion damage. If the damage from an NaClO soak worsens with time and is additionally difficult to detect, using even a relatively short 15-min NaClO soak could result in damage that causes reductions in performance that might not be readily observable. In our study, we were unable to directly observe damage from the NaClO soak to the EP nitinol surface, but the NaClO soak did result in a reduction in fatigue performance as demonstrated by the increased variability in fatigue life.

5. Conclusions

Overall, the results presented herein do not seem to support the generalized use of an NaClO soak because of its lack of effectiveness in identifying inclusions and because it leads to some measurable reductions in performance. The NaClO soak identified only one specimen with surface inclusions and led to the following reductions in performance:

- Increased nickel release on Day 1 for BO nitinol with no change to any other timepoint for either nitinol surface finish
- Decreased fatigue life of BO nitinol and increased variability in fatigue life for both nitinol surface finishes

NaClO soaking appears to modify the surface of nitinol in ways that can be difficult to detect and that result in either similar or reduced performance as compared to controls.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1.
Depth profiles from Auger electron spectroscopy; BO nitinol (left) had an oxide thickness of 651 nm and EP nitinol (right) had an oxide thickness of 11 nm

Fig. 2.
Black flocculent material observed on one of the BO nitinol specimens after the 15-min NaClO soak

Fig. 3. SEM micrographs of nitinol wires before and after NaClO soaking: as-received BO nitinol (top left), NaClO-soaked BO nitinol (top right), as-received EP nitinol (bottom left), NaClO-soaked EP nitinol (bottom right). All wires shown had passed the visual inspection for black flocculent material

EP nitinol As Received

EP nitinol NaClO Soaked

Fig. 4.
SEM micrographs of inclusions along the length of EP nitinol wire after fatigue testing and corresponding EDS spectra of the inclusions

Fig. 5. Representative cyclic potentiodynamic curves from corrosion testing. Arrows indicate the direction of the potentiodynamic scan

Fig. 6. Nickel release over time (Days 1, 2, 7, and 14) for BO (left) and EP (right) nitinol wire. * indicates significant difference between as-received and NaClO-soaked wires

Fig. 7.
S-N curves showing average values for BO nitinol (top) and EP nitinol (bottom)

BO nitinol
As Received

BO nitinol
NaClO Soaked

EP nitinol
As Received

EP nitinol
NaClO Soaked

Fig. 8.

SEM micrographs of fatigue fracture surfaces. The zoomed-out images on the left were taken in secondary mode, while the zoomed-in images on the right were taken with backscatter. The as-received BO nitinol and both EP nitinol conditions have clearly identifiable inclusions at the fatigue crack initiation point. The NaClO-soaked BO nitinol has what appears to be a corrosion pit at its fatigue crack initiation point. This corrosive damage likely occurred during the NaClO soak

Rest potential, breakdown potential, and over potential from cyclic potentiodynamic polarization testing presented as average $\pm$ standard deviation

Table 1

Material	Condition	E_r , mV	E_b , mV	$E_b - E_r$, mV
BO nitinol	As received	-515.4 ± 10.8	-36.3 ± 14.4	479.0 ± 24.0
	NaClO soaked	$-538.8 \pm 18.8^{(a)}$	11.6 ± 49.5	$550.4 \pm 46.4^{(a)}$
EP nitinol	As received	-135.4 ± 7.0	1000.0 ± 0.0	1135.4 ± 7.0
	NaClO soaked	-100.3 ± 34.3	1000.0 ± 0.0	$1100.3 \pm 34.3^{(a)}$

^(a) Indicates statistical significance for a parameter (E_r , E_b , or $E_b - E_r$) at $p < 0.05$ when compared to the as-received condition for a material

Table 2

As-received BO nitinol fatigue test results

Alternating strain, %	1.20	1.00	0.80	0.56
n_1 (minimum)	6084	6948	21,096	60,230,742
n_2	6336	7776	22,068	61,959,427
n_3	6552	8460	23,004	90,117,884
n_4	6696	8640	25,092	100,000,000
n_5	6768	8784	25,236	100,000,000
n_6 (maximum)	7020	8964	32,256	100,000,000
Mean $\pm$ standard deviation	6576 $\pm$ 331	8262 $\pm$ 763	24,792 $\pm$ 4007	85,384,676 $\pm$ 19,207,754
Range (maximum–minimum)	936	2016	11,160	39,769,258
Coefficient of variation	0.05	0.09	0.16	0.22

Specimens n_1 through n_6 are ordered in increasing number of cycles to failure

Table 3

NaClO-soaked BO nitinol fatigue test results

Alternating strain, %	1.20	1.00	0.80	0.56
n_1 (minimum)	1944	4212	7092	8635
n_2	2088	4356	9612	37,034
n_3	3564	7056	10,908	63,475,842
n_4	4320	7740	11,232	75,842,469
n_5	4824	8712	17,028	83,588,865
n_6 (maximum)	5112	8748	19,692	100,000,000
Mean $\pm$ standard deviation	3642 ± 1365	6804 ± 2053	$12,594 \pm 4773$	$53,825,474 \pm 43,324,987$
Range (maximum–minimum)	3168	4536	12,600	99,991,365
Coefficient of variation	0.37	0.30	0.38	0.80

Specimens n_1 through n_6 are ordered in increasing number of cycles to failure

Table 4

As-received EP nitinol fatigue test results

Alternating strain, %	1.20	1.00	0.83	0.69
n_1 (minimum)	6408	13,032	33,880	45,663,344
n_2	8208	13,644	42,890	46,043,393
n_3	8244	13,968	44,973	47,571,290
n_4	9576	14,004	49,862	48,466,805
n_5	10,476	14,940	67,727	66,726,440
n_6 (maximum)	10,656	15,480	77,663	75,859,842
Mean $\pm$ standard deviation	8928 ± 1621	$14,178 \pm 889$	$52,833 \pm 16,535$	$55,055,186 \pm 12,945,165$
Range (maximum–minimum)	4248	2448	43,783	30,196,498
Coefficient of variation	0.18	0.06	0.31	0.24

Specimens n_1 through n_6 are ordered in increasing number of cycles to failure

Table 5

NaClO-soaked EP nitinol fatigue test results

Alternating strain, %	1.20	1.00	0.83	0.69
n_1 (minimum)	8712	12,240	26,347	20,472,797
n_2	8856	13,320	45,870	46,770,570
n_3	9468	13,392	50,402	49,617,236
n_4	9576	14,328	54,002	72,717,128
n_5	9684	16,092	702,345	100,000,000
n_6 (maximum)	10,656	18,288	3,194,407	100,000,000
Mean $\pm$ standard deviation	9492 $\pm$ 695	14,610 $\pm$ 2217	678,896 $\pm$ 1,260,189	64,929,622 $\pm$ 31,815,524
Range (maximum–minimum)	1944	6048	3,168,060	79,527,203
Coefficient of variation	0.07	0.15	1.86	0.49

Specimens n_1 through n_6 are ordered in increasing number of cycles to failure