Corrosion Behavior of NiTiCo High Stiffness Shape Memory Alloys

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Abstract

The corrosion behavior of high stiffness NiTiCo shape memory alloys was systematically investigated in the present study including straight wires, wire formed stents, and laser cut stents. It was found that the corrosion behavior of NiTiCo alloys is comparable to that of binary NiTi. This is attributed to the small amount of cobalt used in the ternary alloy. Additionally, the corrosion resistance of high stiffness NiTiCo shape memory alloys is independent of the stent forming method. To explore the galvanic corrosion susceptibility between NiTiCo and binary NiTi alloys, a NiTi sleeve was laser welded to a NiTiCo stent. There was no galvanic corrosion observed in this NiTiCo-NiTi component even after the component was immersed in a phosphate buffered saline (PBS) solution at 37°C for three months. This study will shed some light on the industrial applications of high stiffness NiTiCo shape memory alloys.

Introduction

Nitinol shape memory alloys (SMAs) have been widely used in both industrial and medical devices. With increasing performance requirements and size restrictions, there is a need to develop high stiffness SMAs, i.e., high modulus and high upper/lower plateau stress. Ternary element alloying to binary NiTi is a useful method to modify the mechanical properties and transformation behaviors of the NiTi [1,2]. Recently, NiTiCo high stiffness SMAs have been developed for industrial and medical device applications [3]. It has been documented that the Co atoms prefer occupying the Ni lattice sites in NiTiCo alloys [1,4]. Fasching et al [3] compared the mechanical properties of NiTiCo alloys to binary NiTi counterparts, and claimed that the Co addition increases the modulus approximately 30% compared to the binary counterparts.

Corrosion resistance and biocompatibility are important characteristics for the application of high stiffness NiTiCo shape memory alloys in medical devices. There are some reports on the biocompatibility and corrosion resistance of NiTiCo alloys. Fasching et al [3] investigated the biocompatibility of electropolished NiTiCo wires using cytotoxicity and hemolysis, and claimed that the biocompatibility performance of NiTiCo alloys is similar to that of NiTi counterparts. Wang and Zheng [5] studied the electrochemical behavior of a $Ti_{50}Ni_{47.2}Co_{2.8}$ orthodontic wire in solutions with different pH values where the ion release was characterized using inductively coupled plasma optical emission spectroscopy. They found that the Co addition had little effect on corrosion behavior. However, the corrosion behaviors of high stiffness NiTiCo SMAs have not been systematically documented yet, especially for completed devices. In the present study, the corrosion behavior of high stiffness NiTiCo SMAs have been systematically investigated including straight annealed wires, wire formed stents, and laser cut stents. The galvanic corrosion between NiTiCo alloys and binary NiTi was also explored. This study will shed some light on the industrial applications of high stiffness NiTiCo shape memory alloys.

Experimental Details

The NiTiCo alloys were fabricated at SAES Smart Materials consistent with ASTM F 2063-05 with the exception of the cobalt addition. The alloys were then processed to 0.45 mm wire and 3.9×4.65 mm tube using Memry standard methods. Three types of samples: straight annealed wires, wire formed stents, and laser cut stents, were then fabricated. All of the samples were electropolished and passivated per ASTM A967-05 before corrosion testing. To investigate the susceptibility of galvanic corrosion between NiTiCo and NiTi, a NiTi sleeve was laser welded to the wire-formed NiTiCo stent. The surface morphology of the samples was characterized using scanning electron microscopy (SEM).

The corrosion resistance testing was conducted in a phosphate buffered saline (PBS) solution at 37°C per ASTM F 2129-08. The PBS solution was de-aerated using pure N2 gas for 30 minutes, the open circuit delay was set as 1 hour, and the scan rate was 0.167 mV/second. The scan was reversed after corrosion or oxygen evolution was detected.

Results and Discussion

Figure 1 compares the corrosion behavior of straight annealed NiTiCo and NiTi wires, which were electropolished and passivated before test. The two potential-current density curves are nearly identical and no pitting was observed up to the point of oxygen evolution. This observation indicates that the corrosion resistance is comparable between NiTi and NiTiCo wires which is consistent with literature [3,5]. The observed breakdown potential is approximately 1 V for each wire which satisfies the requirements for implantable devices, although oxygen evolution is evident at this range. Both wires show repassivation capability and the hysteresis between the forward and reverse scans is very small. This observation indicates that the Co addition has little effect on the corrosion behavior of NiTi alloys although the alloying increases the stiffness and modifies the transformation behavior of NiTi alloys [1,2,3]. This is explained by the limited amount of the Co addition [3].

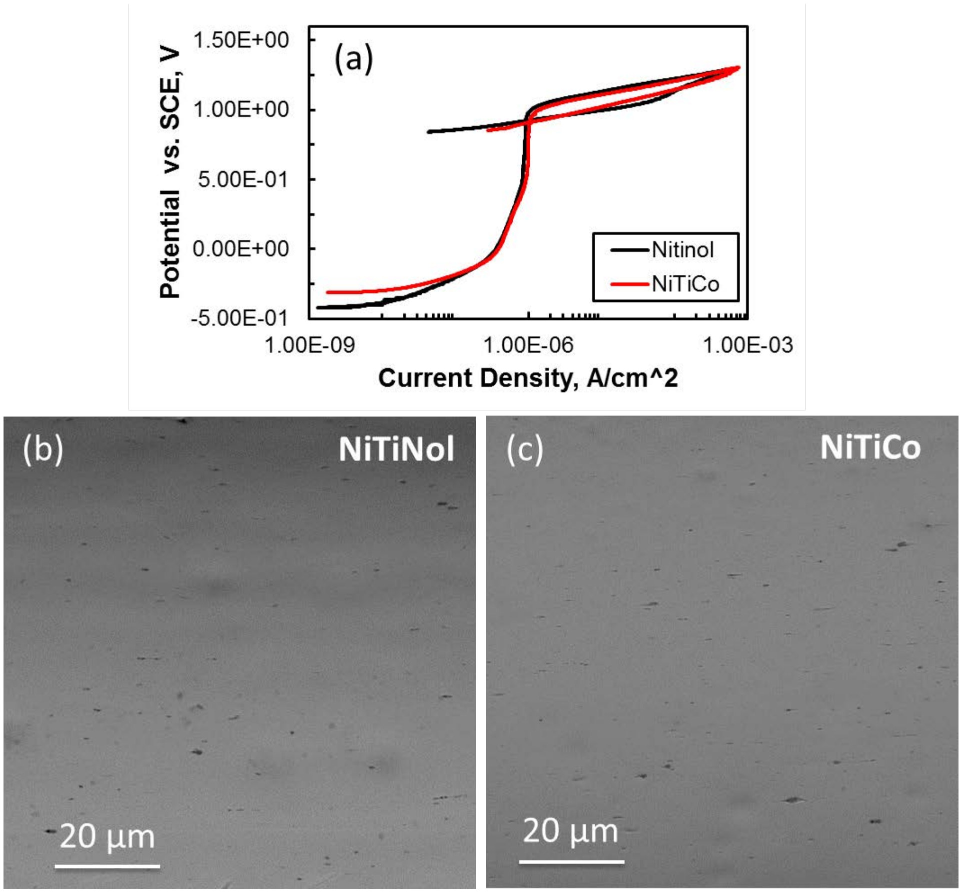

Figure : 1 (a) Comparison of corrosion behavior of straight annealed NiTi and NiTiCo wires, (b) the surface morphology of NiTi wires, and (c) NiTiCo wires.

The surface morphology of the NiTiCo and binary NiTi wires is comparable as Figure 1b and 1c show. The wire drawing direction is horizontal. Some nonmetallic inclusions and stringers exist on both the NiTi and the NiTiCo wire surface.

Currently, there are two main manufacturing methods to produce stents: wire forming and laser cutting. Figure 2 represents the corrosion behavior of wire formed stents from high stiffness NiTiCo SMAs. The corrosion behavior of straight annealed NiTiCo wires is included as well for comparison. Interestingly, their corrosion behavior is similar, indicating that the wire forming process does not change the corrosion behavior. The surface morphology of the NiTiCo stent is shown in Figure 2b, which is comparable to that of straight annealed NiTiCo wire as Figure 1c shows.

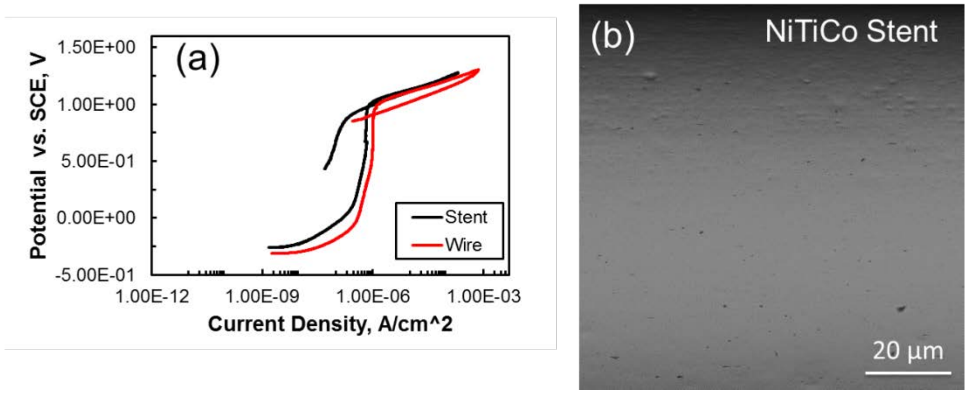

Figure 2: (a) Comparison of corrosion resistance of wire formed stents and straight annealed high stiffness NiTiCo SMAs, and (b) the surface morphology of NiTiCo wire after electro-polishing and passivation.

Laser cutting is another widely used method to manufacture stents from NiTi based shape memory alloys. Figure 3 shows the corrosion behavior of laser cut formed NiTiCo stents. Irrespective of whether shape setting is conducted or not after laser cutting, the corrosion behavior is similar. Additionally, it is comparable to that of wire formed stents and straight annealed NiTiCo wire. This observation further confirms that the stent forming method has no effect on the corrosion behavior of NiTiCo alloys. The breakdown potential is approximately 1 V and is comparable to that from straight wire and wire formed stents. The comparable corrosion behavior between NiTi and NiTiCo alloys is explained by the limited amount of the Co addition which is in the range of ~1-2% [3].

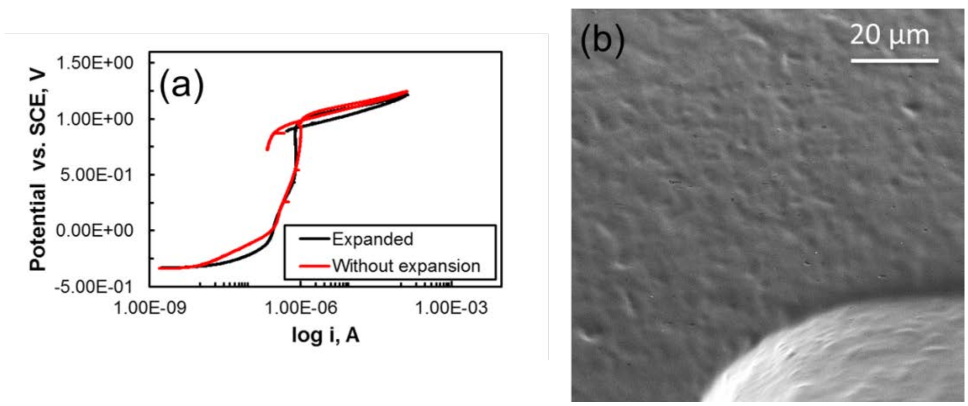

Figure : 3 (a) Comparison of corrosion resistance of laser cut NiTiCo stents, with and without expansion after cutting from NiTiCo tube, and (b) the surface morphology of the laser cut NiTiCo stent.

Galvanic corrosion might occur when two different metals are connected due to differing rest potentials. With a closer observation of Figure 1a, the measured rest potential (E_r) for NiTiCo alloys is slightly higher than that for binary NiTi. To investigate the susceptibility of galvanic corrosion between NiTiCo and NiTi alloys, a NiTi sleeve was laser welded to a wire formed NiTiCo stent [6] as Figure 4a shows. A small gap exists between the core NiTiCo wire and the NiTi sleeve so a crevice corrosion condition has been created in the component. During cyclic potentiodynamic polarization measurement, the corrosion behavior of the component was monitored. It is worthy to note that both galvanic and crevice corrosion affect the measured results since NiTi alloys are susceptible to crevice corrosion as well [7,8]. Figure 4b compares the measured corrosion behavior of NiTiCo-NiTi components. Overall, the corrosion behavior is comparable except that the curve from the NiTiCo-NiTi component shifts to the right slightly. Interestingly, there is no galvanic corrosion or crevice corrosion observed in the present component.

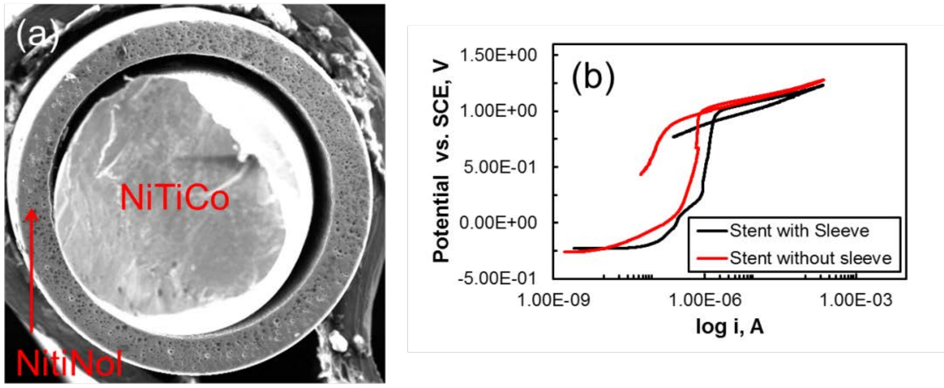

Figure 4: (a) The component of NiTiCo wire formed stent with a laser-welded NiTi sleeve, and (b) Comparison of corrosion behaviors of NiTiCo wire formed stents with or without NiTi sleeves.

Corrosion resistance with long term immersion in a saline environment is required for applications of a NiTiCo stent since implanted stents will remain in the body for a long duration. Recently it has been reported that long term immersion affects both the rest potential and breakdown potential of NiTi wires [9]. To explore the effect of immersion duration on the corrosion behavior of NiTiCo stents, the NiTiCo-NiTi components were immersed in PBS solution at 37°C for different durations. The corrosion behavior was measured per ASTM F 2129-08. Figure 5 presents the corrosion behavior of the components after different durations of immersion in PBS solutions.

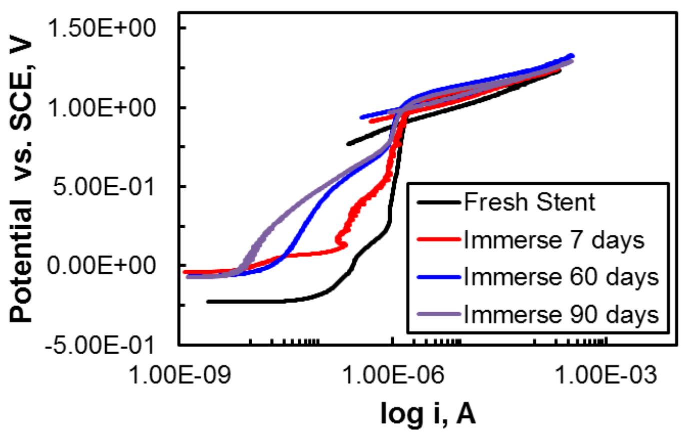

Figure 5: The effect of long term immersion in PBS solution at 37℃ on the corrosion behavior of NiTiCo-NiTi components. For comparison, the corrosion behavior of a fresh component was also plotted.

Long term immersion affects corrosion behavior of the NiTiCo-NiTi components. Firstly, the long term immersion increases the rest potential, E_r, of the NiTiCo-NiTi components initially and then the rest potential is saturated and no longer increases. As Figure 5 shows, the rest potential, E_r, increases from around -200 mV to almost zero after a 7 day immersion. Then it saturates with further immersion duration. Additionally, the long term immersion has almost no effect on the break down potential of the NiTiCo-NiTi components. For the 90 day immersion, the break down potential is approximately 1 V for the measured components which is in the range of oxygen evolution.

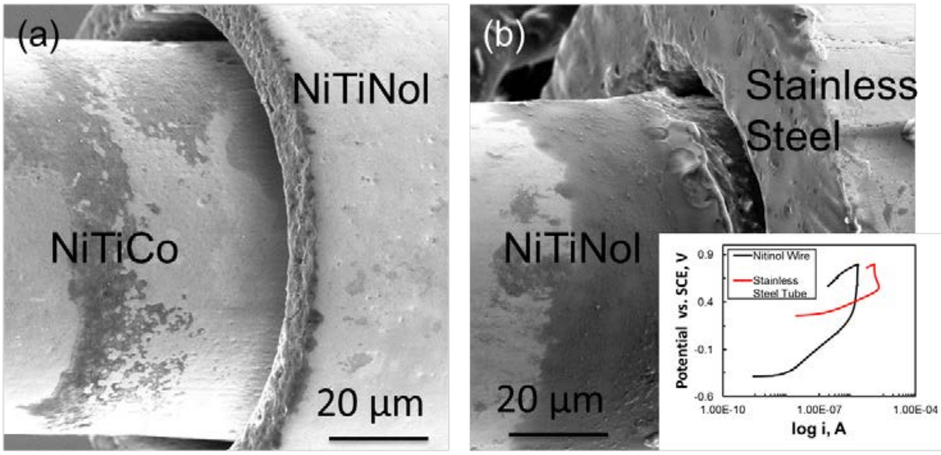

Figure 6: The comparison of galvanic corrosion after cyclic polarization measurements, (a) the NiTiCo-NiTi component after immersion in PBS at 37℃ solution for 60 days, and (b) a fresh NiTi-Stainless Steel component. The inset (b) is the potential vs. current curve of pure NiTi wire and stainless steel tube.

Figure 6 compares the NiTiCo-NiTi and NiTi-Stainless Steel components after cyclic potentiodynamic polarization measurements. For the NiTiCo-NiTi components, there is no galvanic corrosion observed even after the component has been immersed in PBS solution at 37°C for 60 days before measurement. On the contrary, apparent galvanic corrosion has occurred on the fresh NiTi-Stainless Steel component as Figure 6b shows. This observation is likely related to the rest potential difference. As Figure 1a shows, the rest potential difference between pure NiTi and NiTiCo alloys is very limited. However, the rest potential difference between pure NiTi and stainless steel is large as the inset of Figure 6b shows.

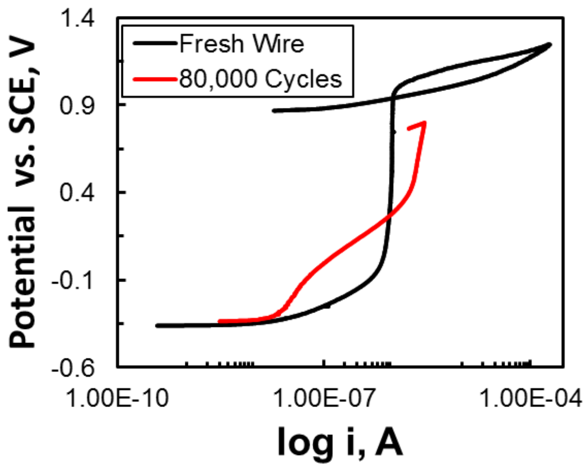

Figure 7: The effect of cycling on the corrosion behavior of NiTiCo wires, where the sample wires were cycled at 0.8% strain for 80,000 cycles before the cyclic potentiodynamic polarization scan.

Fatigue is one of the important characteristics of materials properties. Figure 7 compares the corrosion behavior of NiTiCo wires with and without cycling. The NiTiCo wires were cycled at 0.8% strain for 80,000 cycles before corrosion measurement. Interestingly, the cycling has almost no effect on the rest potential. It is important to note that the wire with cycling was reversed at 800 mV, following the ASTM F 2129-08 standard, while the fresh wire was not reversed until the break down potential was detected. This observation indicates that the corrosion behavior of NiTiCo wire is sufficient for medical device applications after proper treatment.

Summary

The corrosion resistance of NiTiCo alloys was systematically studied in the present study. The following conclusions can be extracted from the experimental results:

(1) The corrosion resistance of NiTiCo alloys is comparable to binary NiTi alloys and the measured breakdown potential is approximately 1 V. This is attributed to the small amount of Co alloying in the ternary NiTiCo alloys.
(2) The method of stent forming does not affect the corrosion resistance of NiTiCo alloys.
(3) There is no galvanic corrosion observed between NiTiCo and binary NiTi alloys.
(4) Long term immersion in PBS increases the rest potential at first and then it is saturated after approximately 7 days and no longer increases.
(5) Cycling at 0.8% strain for 80,000 cycles has little effect on the corrosion behavior of NiTiCo wire.

Acknowledgments

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