An Evaluation of a NiTiCo Alloy and its Suitability for Medical Device Applications

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Abstract

Development of a superelastic material with higher stiffness and plateau stresses than binary nitinol is of interest to the medical device industry because it may allow for lower profile, less intrusive devices without compromising the materials characteristics. This project studied the effect of cobalt (Co) alloying additions on the stiffness and plateau stresses of a superelastic nickel-titanium alloy. In addition, the general physical, mechanical, corrosion and biocompatibility properties of the alloy were compared to binary Nitinol. The results of this study showed cobalt to be an interesting alloying addition that should be considered for future medical devices in applications where stiffness is of concern.

Keywords

Nitinol, high stiffness nitinol, strain-life curves, NiTiCo, corrosion, biocompatibility, superelastic

Introduction

Ternary alloy formulations are not new for nitinol alloys, the dental industry was interested in NiTiCo alloys thirty-five years ago. Several researchers studied the effect of alloying additions which include: gold (Au), palladium (Pd), cobalt (Co), manganese (Mn), and zirconium (Zr) 2 . The transformation and mechanical properties of Ni-Ti-Co alloys have also been examimed. Hosoda et al. and Kishi et al. showed that Co additions increase the yield strength and decrease the M_s of the alloys. In alloys with ternary additions of Co, it is believed that Co occupies Ni lattice sites. Cobalt is well accepted as an implantable element and as such is the focus of this investigation.

An on-going alloy development program at SAES Smart Materials (SSM) resulted in the creation of a family of superelastic alloys with increased modulus (i.e. high stiffness nitinol). One of these new alloys contained minor cobalt additions. The purpose of this project was to compare basic mechanical and physical properties between a standard body-

temperature binary NiTi alloy and a ternary NiTiCo alloy. The scope of this study was to collect data useful for medical device applications.

Experimental Procedure

A NiTiCo ingot was fabricated at SAES Smart Materials with a chemical composition consistent with ASTM F 2063-05 for standard binary nitinol with the exception of cobalt (Co) content. Cobalt ranges between 1-2 atomic percent for this alloy. All of the samples for this study were produced from one lot of 0.052" diameter wire which was cold worked and drawn to a final diameter of 0.015". Where comparisons are made between the NiTiCo alloy and binary nitinol, Nitinol Alloy BB (50.8 at% Ni) was used.

Inclusion analysis was conducted in accordance with ASTM-F2063. Samples were not available in the mill product as specified by ASTM F2063; so the measurements were made on sections of 0.105"-diameter and compared to similar size binary NiTi. Differential Scanning Calorimeter (DSC) tests were conducted on cold worked and shape set parts per ASTM F 2004-3 to determine transformation temperature with an Instrument Specialists DSC 550.

The bending modulus was measured via 3-point bend test using a MTS SinTech with a 2 kip load cell. Tests were conducted at room temperature using 0.04" diameter wire. Figure 1 describes how the bending modulus was measured on each sample.

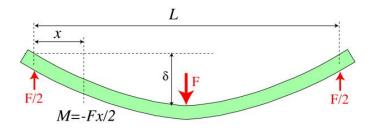


Figure 1: A load, F, was applied to the specimen in order to obtain a predetermined displacement of δ . On the loading cycle the load plateau was measured and when the load was removed the unload plateau was measured.

Tensile tests were conducted on an Instron 5565 load frame with a 5kN load cell as per ASTM F 2516-05. Tensile tests to failure (TTF) and 6% strain tests were performed on straight, shape-set wire samples. Ten samples were tested and averaged for the final results. Ten-cycle load/unload tensile tests were loaded to 6% strain and unloaded with all other test parameters per ASTM F2516-05.

Fatigue testing was conducted using a rotating beam fatigue tester (RBT) with a zero mean, 0.8% maximum alternating strain. The samples were rotated at a constant speed guided in a test block machined with a radius to provide the desired level of strain. The fixture can test up to 10 samples at a time and counts revolutions on each sample individually using a laser counter.

The RBT test is designed to provide comparative results for materials processed with different parameters at the same or varying strain levels. Tests were performed in a circulating 37°C water bath at 1000 RPM to eliminate any heating effect created in the specimen due to dissipative processes during cyclic loading (cyclic stress induced formation of martensite). The heat transfer from the specimen to the test environment helps to counteract this process.

Fatigue curves showing strain versus number of cycles to failure (Strain-N) were generated for etched and electropolished wire and tested with the rotating beam tester described above. Test blocks were made to provide strains of 2.3%, 1.8%, 1.0%, 0.8%, and 0.65%. Three samples of each wire size were tested at each strain level. The test was run to failure or suspended at 10 million cycles.

Potentiodynamic polarization tests were performed on electropolished wire samples in accordance with ASTM F2129. The rest potential (E_r) was monitored for one hour after immersion of each sample, and the potentiodynamic scan was then performed at a rate of 1.0 mV/s. In each case, the potential scan was started from E_r and, if breakdown did not occur, was continued up to a vertex potential (E_v) of approximately 0.8 V (SCE). The polarization tests and open circuit potential measurements were performed using a computer-controlled electrochemical testing system (Gamry Instruments). All potentials were measured with respect to a saturated calomel electrode (SCE). A graphite rod was used as a counter electrode for the polarization tests.

Standard biocompatibility tests were run to determine if the presence of cobalt would affect the overall biocompatibility of the NiTiCo alloy. Two basic tests were selected and sent to an outside laboratory for analysis. The first test, cytotoxicity (ISO 10993-5), is known for being a rapid, standardized test that is sensitive and inexpensive. The results determine whether sample contains significant quantities of harmful extractables (i.e. Ni, Co) and what their effect may have on cellular components. The second test, hemolysis (ASTM F756-08), determines compatibility of devices designed for direct or indirect contact with circulating blood. Affectively, hemolysis measures the ability of a material to cause red blood cells to rupture. Electropolished 0.021" diameter NiTiCo and binary NiTi wire we evaluated for biocompatibility.

Results and Discussion

Basic transformation and inclusion properties were measured on the NiTiCo alloy and are compared to binary NiTi in Table 1. As stated previously, Co additions have been shown to lower the transition temperature of nitinol alloys. NiTiCo alloys with warmer transition temperatures are also in development but will not be discussed in this study. The maximum inclusion size and area fraction in the longitudinal direction for the NiTiCo alloy was well within the specification. Typical results for a binary NiTi alloy at the redraw stage are also reported. For this particular ingot, the NiTiCo alloy exhibited significantly smaller maximum inclusion size than the binary alloy; however, it is not uncommon to observe a binary alloy with a maximum inclusion size in a range similar to the NiTiCo alloy examined in this study.

Table 1. Summary of Ingot properties of binary NiTi and NiTiCo

Property	Binary NiTi	NiTiCo
As (fully annealed ingot) [°C]	-15	-80
Af (fully annealed redraw wire) [°C]	+5 ±10	-67
Maximum Inclusion Length (µm)	19.77	11.34
Maximum Inclusion Area Fraction (%)	0.97	0.71

Tensile data was collected on ten samples and averaged and summarized in Table 2. Exemplar stress-strain curves for binary NiTi and NiTiCo, are shown in Figures 2 and 3 respectively. The results were very consistent between samples and showed similar ultimate tensile strength between NiTiCo and binary NiTi alloy. The upper and lower plateau increased significantly in the NiTiCo alloy compared to binary; however, the difference between the upper and lower plateau was the same for both alloys (~39ksi). NiTiCo exhibited approximately three times the residual strain. The upper, lower and UTS values for the NiTiCo alloy are approximately 30% higher than for the traditional binary alloy.

Ten cycle load/unload curves were made to examine the change in hysteresis loop over several cycles. Figures 4 and 5 show the ten-cycle test. A lowering of the upper plateau and an increase in permanent set with cycling was observed for both alloys, however the decrease was more pronounced in the NiTiCo. A full 6% strain was still achievable for both alloys after 10 cycles. Cyclic degradation of mechanical properties is typical of nitinol alloys; Heckmann showed that there is a strong effect of the thermomechanical processing on the stability of the alloy⁴. A study of different thermomechanical treatments is underway to optimize of the properties of the NiTiCo alloys.

Table 2. Mechanical property comparison between binary NiTi and NiTiCo.

Property	Binary NiTi	NiTiCo
Loading plateau stress @ 3%	492 MPa	710 MPa
strain, in Austenite	(71.3ksi)	(103 ksi)
Unloading plateau stress @	226 MPa	439 MPa
3% strain, in Austenite	(32.8 ksi)	(63.7 ksi)
UTS in Austenite	1320 MPa	1320 MPa
U13 III Austeinte	(191ksi)	(191 ksi)
Max. residual elongation	0.1	0.3
after 6% strain in Austenite	0.1	0.3
Bending Modulus (3-point	60 ksi	85ksi
bend)	OU KSI	o SKSI

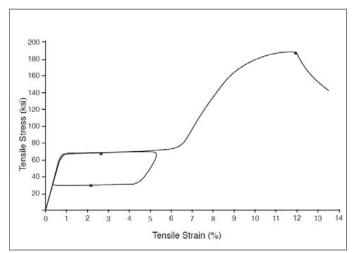


Figure 2. Typical stress-stain curve for binary nitinol alloys.

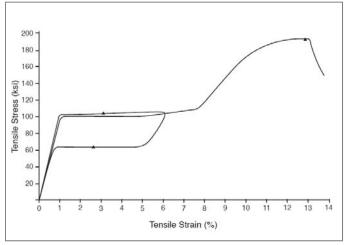


Figure 3. Typical stress-strain curve for high-stiffness NiTiCo alloys.

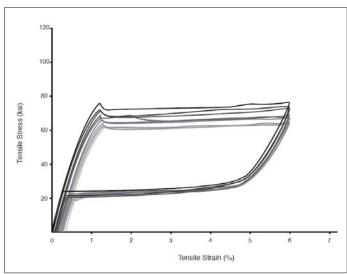


Figure 4. Ten-cycle load/unload curve for binary nitinol, only minor ratcheting apparent.

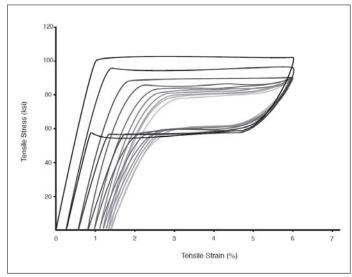


Figure 5. Ten-cycle load/unload curve for NiTiCo, exhibits some ratcheting.

The fatigue data plotted in Figure 6 represents 3 samples per strain level and 5 strain conditions; all data points are plotted in the Strain-N graph. NiTiCo showed a decrease in fatigue life over NiTi when tested in low cycle strain control. At high cycles there was no difference between the alloys and both showed evidence of an endurance limit. The decreased low cycle fatigue can be attributed to the higher upper plateau of NiTiCo alloy as compared to the binary NiTi alloy. For a given strain level, the stress level will be lower in the alloy with the lower plateau than the one with the higher plateau. The lines converge at higher cycles because the strain levels are low enough to remain in the linear elastic region for both alloys.

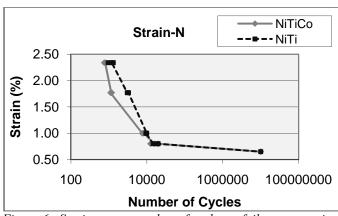


Figure 6. Strain versus number of cycles to failure comparing NiTiCo to binary NiTi.

Cyclic polarization scans were performed on electropolished and passivated wire samples to determine the pitting corrosion performance of the wire. An example of the polarization results for NiTiCo is shown in Figure 7. No breakdown was observed in any of the NiTiCo or binary NiTi samples tested. No breakdown means the sample did not exhibit pitting corrosion during the test cycle; this corresponds to a high level of corrosion resistance. Similar electropolished and passivated binary NiTi wire also did not breakdown during the ASTM F2129 tests.

Cytotoxicity is the quality of being toxic to cells. Cytotoxicity testing was performed using the MEM elution method to evaluate the toxicity or irritancy potential of the material in vivo. In addition to the NiTiCo samples, NiTi material was also submitted to act as a baseline reference. Both the binary nitinol and NiTiCo wires scored zero, or no reactivity according to the qualitative evaluation of the cells exposed to the extracts. ISO specifications state that a numerical grade of 2 or greater is considered to have a cytotoxic effect.

Hemolysis determines compatibility of devices designed for direct or indirect contact with circulating blood. The test measures the ability of a material to cause red blood cells to rupture. The hemolytic grades for the test article and positive control are assigned by ASTM F756-08. The corrected hemolytic index for the binary nitinol and NiTiCo test articles was zero. Therefore, the test article is considered non-hemolytic by the direct contact method according to the hemolytic grading criteria in the ASTM F756-08 standard.

Conclusions

- NiTiCo alloy has a: 30% higher modulus, 35% higher Loading Plateau and 33% higher Unloading Plateau when compared to the binary alloy.
- Fatigue tests resulted in similar strain-life curves to binary NiTi, when tested in stain controlled, zero mean strain rotating beam testing.
- Electropolished and passivated NiTiCo wire did not exhibit breakdown when subjected to potentiodynamic

- polarization testing as per ASTM F2129. NiTiCo has similar corrosion resistance to binary NiTi.
- Biocompatibility performance is similar between NiTi and NiTiCo and exhibited no reactivity in both the cytotoxicity and hemolysis tests performed in this study.

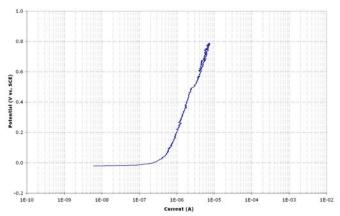


Figure 7. Cyclic potentiodynamic polarization data for NiTiCo showing no breakdown.

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