Optimization of Melt Chemistry and Properties of 35Cobalt-35Nickel -20Chromium-10Molybdenum Alloy Medical Grade Wire

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Abstract

The end use requirements for standard ASTM F 562 wire for pacing leads present difficult challenges to achieve the desired performance of these permanent implant devices. It will be shown that an optimized process produces a measurable improvement in surface finish and greatly improved fatigue life of wire forms under various conditions pertinent to the medical device industry. The purpose of this paper is to review the property improvements of ASTM F 562 wire. The improved material, called 35N LT™ alloy, meets all chemical, mechanical, and metallurgical requirements of the ASTM F 562 specification, and other specifications based on that document. The chemistry of 35N LT alloy falls within the ranges established for UNS designation R30035.

Introduction

The role of material science, particularly metallurgy, in biomedical implants has grown considerably in recent years. Increasing performance is always the engineer's objective. In these applications the goals set for the metallurgist are familiar: increasing strength, maintaining ductility and increasing fatigue life. The guiding paradigm: Processing → Structure → Properties → Performance provides the framework through which these goals are achieved. For pacing leads, an increase in fatigue life is the desired property improvement. Achieving this property enhancement requires tailoring the upstream processing to produce a more fatigue resistant microstructure.

Background

The principal failure mechanism is fatigue initiation at large, cubical TiN particles. These nitrides do not break up over the course of thermomechanical processing and, in fact, retain their as-cast size into the final product. In addition, their presence causes surface defects on the wire since large nitrides damage the die during the drawing process, greatly reducing yield[1].

An improved process was developed which overcomes these limitations. This report describes the improvement in microcleanliness, surface defect density and fatigue life.

Experimental Procedure

Processing

Materials for this investigation were provided as 3,000-pound VIM electrodes which were VAR remelted into 17" diameter ingots. The VAR ingot was homogenized to reduce microsegregation, then rotary forged on a GFM machine to produce 4"∅ billet which was subsequently hot rolled on a continuous rolling mill to 0.219"∅ coil. The coil was annealed, shaved to 0.216"∅ and pickled in preparation for drawing.

Drawing was accomplished using carbide dies and powder lubricants to 0.064". Additional processing to the final diameter of 0.007" was completed in diamond dies using mineral oil lubricants. For evaluation of the new material, the final wire diameter was set at 0.007" +/- 0.0002" with the goal of maintaining an ultimate tensile strength of 300 to 320 ksi.

Testing

Microcleanliness Evaluation Procedure: An historical survey of eight (8) ASTM F 562 standard samples were cut at 0.100" diameter hard drawn material. These samples represented five (5) melted master heats. Two (2) samples of 35N LT alloy were cut from 1.000" and 0.216" diameter hot rolled and annealed material. Both 35N LT samples were from the same melted master heat. The samples were then mounted in a thermosetting compound to provide a longitudinal section through the entire length of each segment. The mounted specimens were ground and polished metallographically to obtain a polished plane near the longitudinal center of the samples.

The prepared sections were examined in a scanning electron microscope (SEM) using backscattered electron imaging (BEI). For each sample section, 160 images showing a representative area of the prepared section were acquired at a magnification of 1000X for a total examined area of 1.77 mm^2 per sample.

Analysis of features appearing darker or brighter than the background was conducted using image analysis software. Contrast was adjusted so that features having a higher mean atomic number than the matrix would appear brighter compared with those features having a lower mean atomic number which would appear darker. The largest dimension was recorded for each individual feature in each of the images. The inclusions were categorized by largest dimension into 1 µm groups up to the largest inclusion detected. Some largest dimension measurements could be the result of a discrete inclusion occurring in a "stringer" formation but not discernable as an individual inclusion. Features smaller than 0.2 µm were not counted. This analysis was performed on all 1600 images. In this way a direct comparison of cleanliness between the standard ASTM F 562 and 35N LT material types was accomplished.

Selected inclusions were examined at higher magnifications, and qualitative chemical analysis was performed on the inclusion by energy dispersive x-ray spectroscopy (EDS).

Grain Size Testing

A grain size analysis was performed against the standard ASTM F 562 material to confirm similarity of the new alloy. The grain size was determined using the Abrams three circle intercept procedure described in ASTM E 112. Samples were taken at the process anneal size (.0106”) for the .007” finish wire.

Surface Analysis Procedure

Visual Examination: For both standard ASTM F 562 and 35N LT 0.007” wire, three separate fifteen-foot samples were obtained. Each sample was visually rated at a magnification of 45X in three datasets at the beginning, middle, and end of the sample. Each dataset consisted of four adjacent one-foot sections. Each section was rated to the following criteria: 1 = accept, 2 = marginal acceptance, 3 = marginal reject, 4 = reject, and 5 = gross reject. Level of acceptability was based on current demand in the cardiovascular market for surface integrity on implantable wire products.

Eddy Current Examination: Fourteen 1000-foot sections of standard ASTM F 562 alloy wire and sixteen 1000-foot sections of 35N LT alloy 0.007” wire were evaluated with eddy current sensors. A detection threshold was set that would intercept naturally occurring eddy current field signals (*Hs*) with a skewed right distribution in signal size. The skewed size distribution of Hs signals is typical of naturally occurring surface and exposed subsurface features on a wire. The standard ASTM F 562 alloy wire was used as a baseline. The number of over threshold signals per 1000-foot section was counted in order to characterize the typical surface variation of all thirty samples.

Mechanical Properties Testing

Tension Testing: Tensile properties were measured according to the latest revision of ASTM E 8, Standard Test Methods for Tension Testing Metallic Materials.

Fatigue Testing: Wire samples were submitted for accelerated fatigue testing using rotary beam cycle testing. The goal was to establish the endurance limit of each material type. Results from this accelerated testing have historically shown good correlation to coil flex life testing[2]. Rotary beam testing places the sample under cyclic tensile and compressive stresses. During each rotation, the part of the specimen in tension will go into compression and back to tension so that the stresses are completely reversed. The high cycle rate of 3600 rpm produces very repeatable results. Samples were tested by positioning a cut length of material at a specified radius to obtain a desired stress level. Seven samples were tested at each stress level. A failure occurs when the wire breaks. The testing equipment senses the wire break and records the length of the test in minutes.

Experimental Results

Microcleanliness Evaluation: A direct comparison of cleanliness between the standard ASTM F 562 and 35N LT material types was accomplished by evaluating the frequency distribution of inclusion feature size in the 1 μm groups for the median size inclusion and 99th percentile inclusion feature limit. The largest inclusion feature size was found for each sample. The total number of inclusion features for each sample was evaluated for the mean and standard deviation for both material types.

Table 1. Inclusion feature size distributions for standard ASTM F 562 and 35N LT alloy wire.

Process Type	Median Inclusion Size, μm	99th Percentile Inclusion Limit, μm	Total Inclusions Found, Mean	Total Inclusions Found, Std. Dev.	Largest Inclusion Found, Mean, μm	Largest Inclusion Found, σ, μm
ASTM F 562 Standard	0.5	6.34	1623	435	31.98	18.83
35N LT Alloy	0.5	3.43	668	279	4.20	0.71

All samples contained features that appeared brighter or darker than the bulk material using BEI. Darker features have a rounded morphology and are typically randomly scattered throughout the sample. The majority of the darker features were inclusions with high concentrations of magnesium and oxide. Some inclusions also contain sulfur. Typical EDS spectra for the dark inclusions are shown below in Figure 1.

The size of a typical inclusion feature in 35N LT alloy wire is seen in image 1, while image 2 shows the largest inclusion feature found in the 35N LT alloy survey.

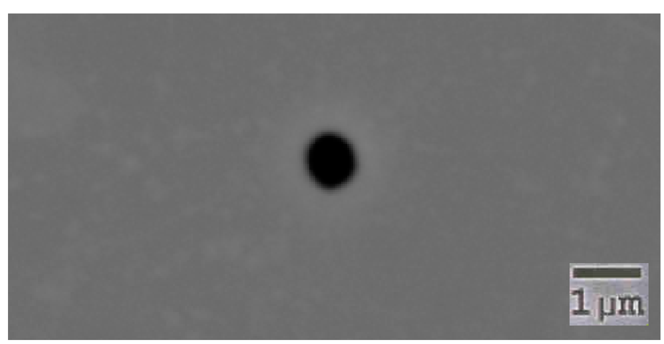


Image 1. BEI of a typical 35N LT alloy inclusion feature.

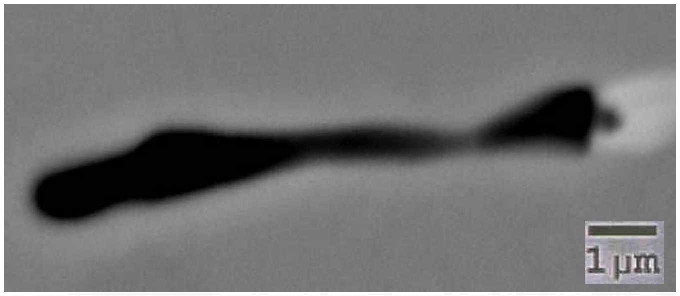


Image 2. BEI of largest inclusion feature in the 35N LT alloy survey.

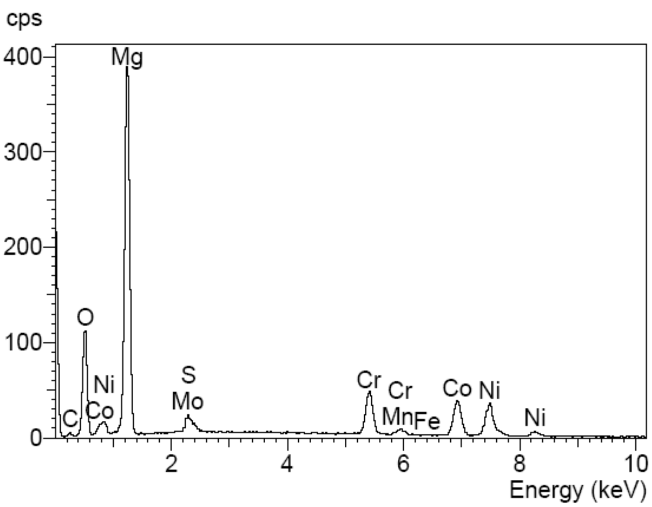


Figure 1. EDS spectra for dark inclusion in 35N LT alloy.

An example of features brighter than the background is shown in Image 3. These features are of a rounded morphology, and exist randomly and in stringers. Many of the largest features are adjoining bright inclusions.

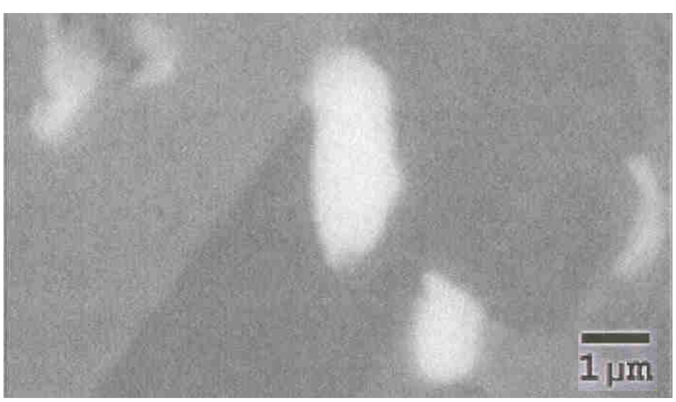


Image 3. BEI of a bright inclusion in 35N LT alloy.

EDS spectra of the bright features detected high concentrations of molybdenum and boron. Typical EDS spectra for the bright inclusions are shown below in Figure 2. Due to the small size of the inclusions, the analysis is a composite of the inclusions and surrounding base metal.

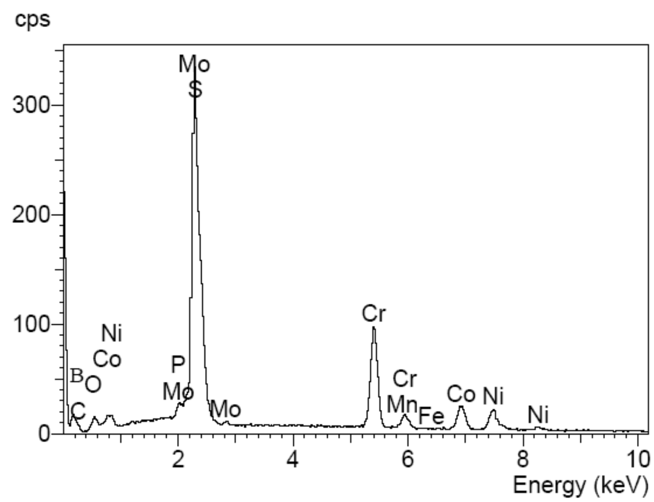


Figure 2. EDS spectra for bright inclusions in 35N LT alloy wire.

In ASTM F 562 standard wire, the largest features are stringers of multiple or broken up inclusions. The inclusions with the greatest frequency are typically submicron inclusions that are randomly scattered throughout the field. The majority of darker features are inclusions with high concentrations of titanium and nitrogen. Some of the darker features consist of a center that is high in magnesium, aluminum, and oxygen with an outer region containing titanium and nitrogen. Other darker features are inclusions with high concentrations of magnesium and/or aluminum along with oxygen.

Images 4 and 5 represent typical over median size inclusion features present in standard ASTM F 562 material. Note that these images are 10 to 20 times lower in magnification than Images 1 and 2.

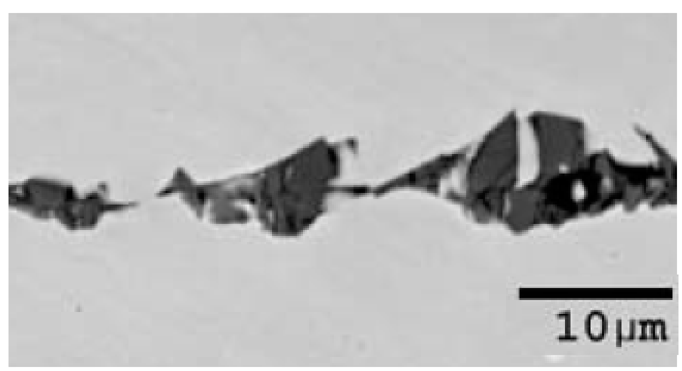


Image 4. BEI of typical over median size inclusion feature in standard ASTM F 562 material.

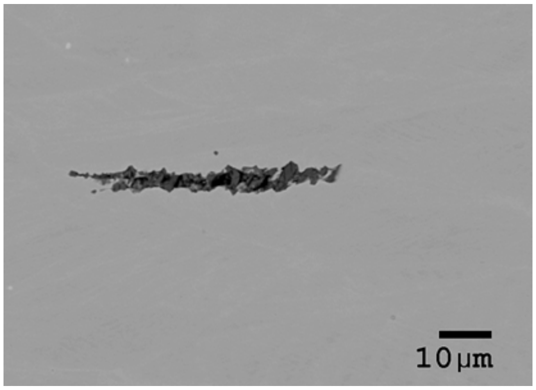
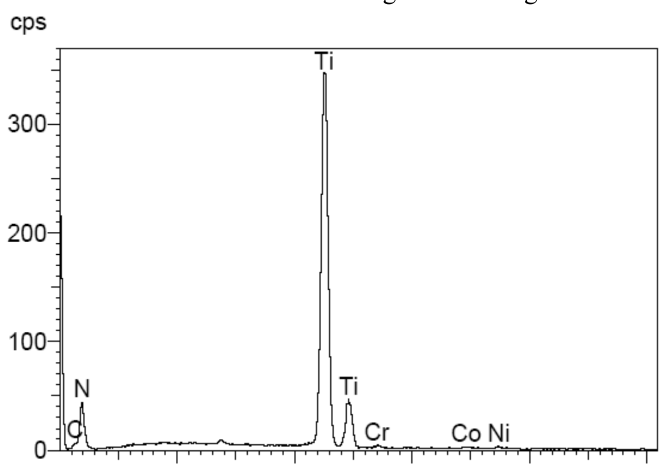


Image 5. BEI of the largest dark inclusion feature in ASTM F 562 material.

The typical EDS spectra of dark inclusions in standard ASTM F 562 wire are shown in Figure 3 and Figure 4.



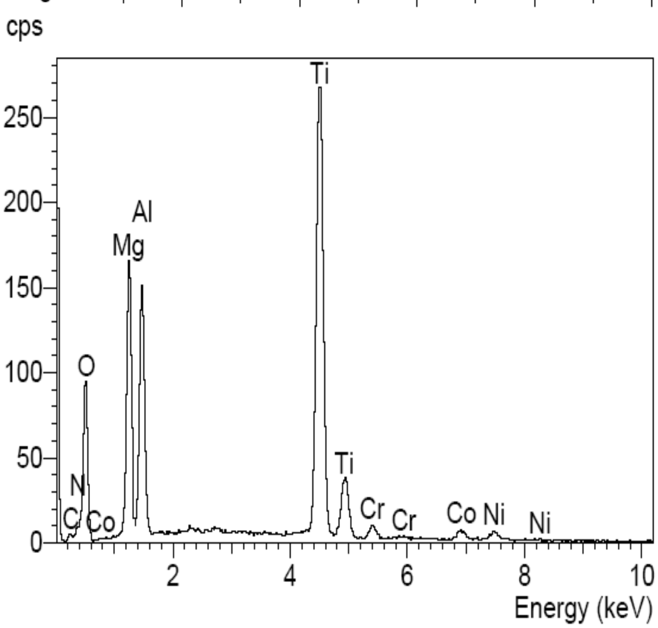


Figure 4. EDS spectra of darker center region of inclusion in ASTM F 562 standard wire.

The features brighter than the background in ASTM F 562 standard wire are rounded. These features are found in stringers, and are randomly scattered. Some clusters of bright features are also observed. Many of the largest features adjoin bright inclusions. EDS analysis of the bright features indicates high concentrations of molybdenum and boron, as shown in Figure 5. Due to the small size of the inclusions, the analysis is a composite of the inclusions and the surrounding base metal.

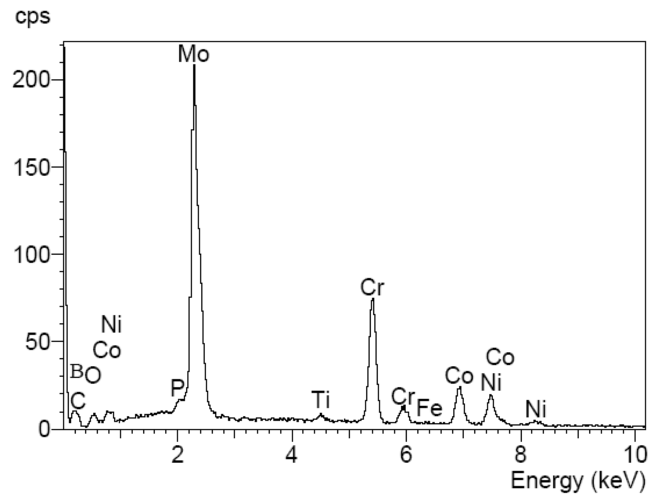


Figure 5. EDS spectra of typical bright inclusion in ASTM F 562 standard wire.

Chemistry for the ASTM F 562 standard is compared with chemistry for the new 35N LT alloy in Table 2, below.

Table 2. Chemistry comparisons between standard ASTM F 562 and 35N LT alloy.

Element	ASTM F 562		35N LT Alloy
	Min.	Max.	
Carbon	-	0.025	0.006
Manganese	-	0.15	0.01
Silicon	-	0.15	0.01
Phosphorus	-	0.015	0.003
Sulfur	-	0.010	0.0006
Chromium	19.0	21.0	20.06
Nickel	33.0	37.0	36.75
Molybdenum	9.0	10.5	10.32
Iron	-	1.0	0.12
Titanium	-	1.0	0.01
Boron	-	0.015	0.008
Cobalt	Bal.	Bal.	32.56

Grain Size Test Results

Test results indicate that the new 35N LT alloy system maintains the desired grain size properties and is similar to the existing alloy. Table 3, together with Figures 6-9, summarizes these results.

Table 3. Grain Size test results.

Grain Size	ASTM F 562 Alloy	35N LT Alloy
Longitudinal	14.6	14.3
Transverse	14.5	14.4

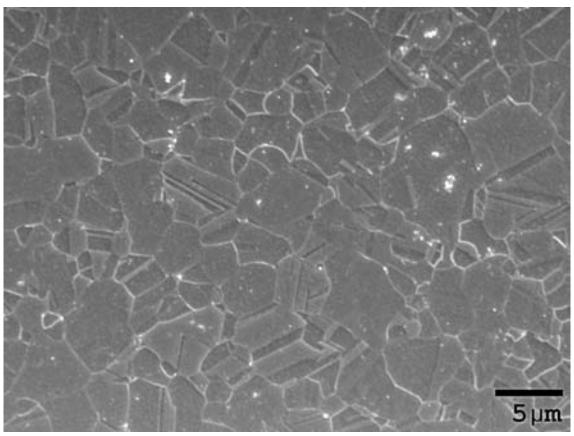


Figure 6. ASTM F 562 Alloy, Longitudinal.

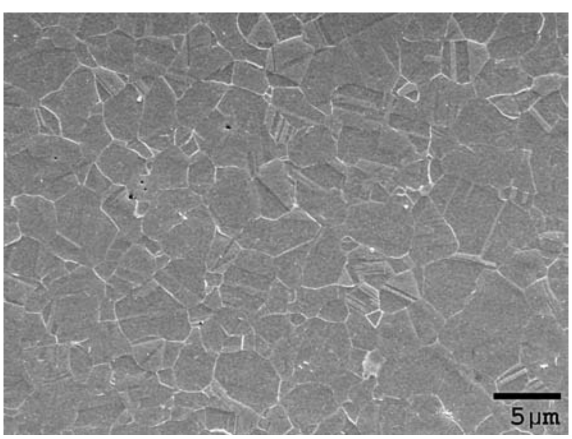


Figure 7. ASTM F 562 Alloy, Transverse.

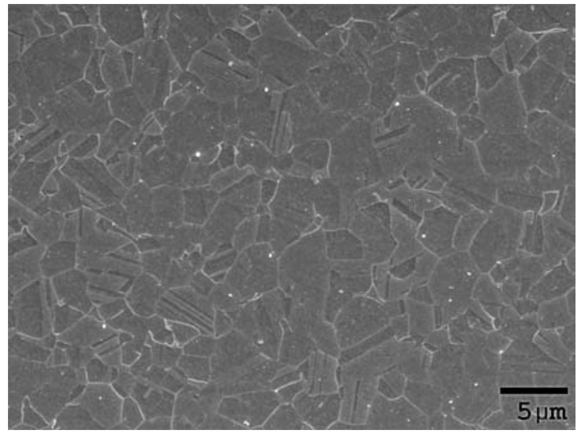


Figure 8. Alloy 35N LT Alloy, Longitudinal.

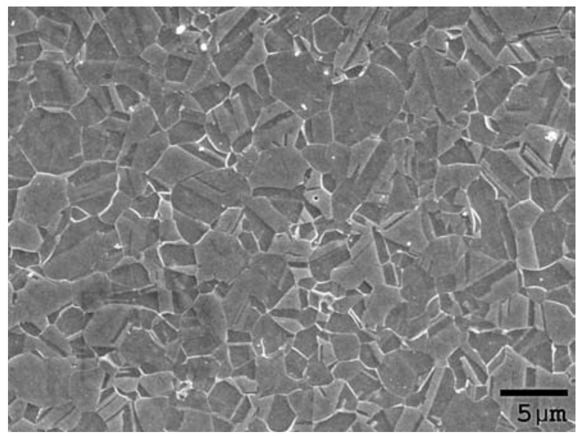


Figure 9. Alloy 35N LT Alloy, Transverse.

Surface Analysis Results

Visual Rating Analysis: Interpretation of the average visual rating per foot data shows a 46% improvement in surface performance of 35N LT wire when compared with standard ASTM F 562 material. Interpretation of the average standard deviation in ratings between one-foot sections indicate a 54% improvement in surface consistency of 35N LT wire compared with standard ASTM F 562 material. The range for over threshold signals between 1000’ sections shows a 65% improvement in surface consistency of 35N LT wire compared with standard ASTM F 562 material.

Table 4 summarizes comparative statistics between standard ASTM F 562 and 35N LT alloy wire data.

Table 4. Visual Rating Results

Process Type	Number of 1 ft. Sections Evaluated	Average Rating	Average Std. Deviations Between 1 ft. Sections
ASTM F 562 Standard	36	2.50	1.58
35N LT Alloy	36	1.36	0.72

Eddy Current Analysis: Interpretation of the average over threshold signals per 1000 feet data indicate a 69% improvement in surface and subsurface performance of 35N LT alloy wire when compared with standard ASTM F 562 wire. Interpolation of the average range for over threshold signals between 1000 ft. sections show a 65% improvement in surface consistency of 35N LT wire when compared with standard ASTM F 562 wire. Table 5 summarizes comparative statistics between standard ASTM F 562 alloy wire and 35N LT alloy wire.

Table 5. Eddy Current Results

Process Type	Number of 1 ft. Sections Evaluated	Average Over-Threshold Signals per 1000 ft.	Average Range Over-Threshold Signals between 1000 ft. Sections
ASTM F 562 Standard	14	2.714	2.538
35N LT Alloy	16	0.8325	0.875

Mechanical Properties

Tension Testing: Tensile properties of standard ASTM F 562 alloy wire and 35N LT alloy wire are comparable, as seen in Table 6. Test results were obtained using 200 lb. load cell, 10" gage length, and a 5 in./min/min cross head speed on an Instron model 4469 system.

Table 6. Summary of tension testing results.

Process Type	ASTM F 562 Alloy	35N LT Alloy
Diameter, in.	0.00695	0.00695
UTS, ksi.	307.6	313.2
YS, ksi.	287.6	284.7
EL, %	2.9	3.1

Fatigue Testing: Valley Instruments rotary beam testers, model 10040, were used for these monofilament wire evaluations. These instruments have a single drive chuck system. Testing was performed in air at 65-75 degrees F. A "runout" is defined as 54 million cycles (15,000 minutes) without a wire break. The test results are presented in Table 7.

Table 7. The average number of cycles to failure.

Stress Value	ASTM F 562 Alloy	35N LT Alloy
250 ksi.	11,130	9,590
200 ksi.	27,070	33,780
150 ksi.	86,530	144,900
125 ksi.	218,700	9,835,000
110 ksi.	1,154,000	33,470,000
100 ksi.	6,774,000	54,000,000
90 ksi.	17,610,000	Not tested *

* Since all seven samples of the 35N LT alloy reached the sensor point of 54 million cycles at the 100 ksi. stress level, no tests were performed at the 90 ksi. stress level.

Beginning with the relatively high stress level of 200 ksi, the improvement achieved by the 35N LT Alloy is evident. The improvement continues and is most dramatic nearer the actual in-use range of 100 ksi. Figure 10 illustrates these data arranged in the typical S-N curve format.

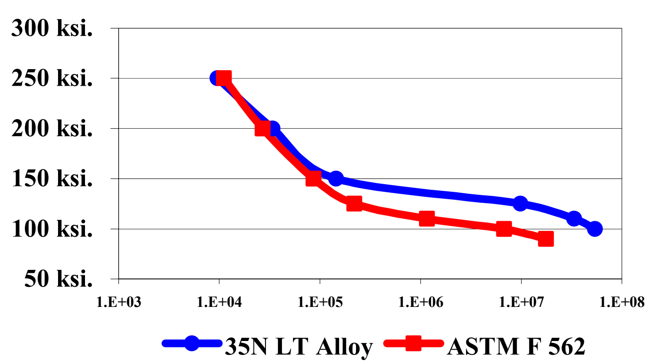


Figure 10. S-N Plot of Data Presented in Table 7.

The goal of fatigue testing is to establish the endurance limit of the material[3,4] . The endurance limit of a metal is the limiting stress below which the metal will theoretically withstand an infinitely large number of cycles without fracture.

Conclusion

An optimized process has been developed that results in a measurable improvement in surface finish, greatly increased fatigue life, and improved microcleanliness in the new 35N LT alloy wire when compared with the standard ASTM F 562 alloy wire.

The most significant conclusion regarding the fatigue testing of the new 35N LT alloy is the establishment of an endurance limit much greater than the existing ASTM F 562 material. The fatigue testing has established an endurance limit that is at least 10,000 psi. greater than any prior testing performed on ASTM F 562 material. This greater fatigue life offers additional safety margins and confidence levels for the medical device design engineer. Two major factors contributing to the stress applied to the wire in a pacing coil are the coil diameter and the wire diameter. The higher endurance limit of the 35N LT Alloy material may allow the design of smaller diameter coils, or the use of a smaller diameter wire, while maintaining the same design safety margin. The test results confirm the improvement in fatigue life of this new alloy system by at least 797% at the 100 ksi stress level.

References

1. Kay, Lawrence, private communication.
2. Per Enghag, Steel Wire Technology, Ch. 3, Materials Testing.
3. Fehring, Thomas K., et al., U.S. Patent No. 6,187,045, “Enhanced biocompatible implants and alloys, February 13, 2001.
4. Fehring, Thomas K., et al., U.S. Patent No. 6,539,607 B1, “Enhanced biocompatible implants and alloys, April 1, 2001.

