Optimization of Melt Chemistry and Properties of Drawn Filled Tube (DFT®) composite materials of 35Cobalt-35Nickel-20Chromium-10Molybdenum alloy (UNS R30035) Medical Grade Wire with Silver core

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Abstract

The end use requirements for Drawn Filled Tube (DFT®) wire for bio-conductor leads present difficult challenges to achieve the desired performance of these permanent implant devices. This composite wire uses an outer layer of ASTM F562 (cobalt-nickel-chromium-molybdenum alloy) material for strength and corrosion resistance combined with a core material of silver to provide high conductivity properties. The purpose of this paper is to review the property improvements of this alloyed wire through the use of enhanced melting chemistry. The new chemistry is the 35N LT® material which meets the requirements of ASTM F 562. It will be shown that the reduction in titanium content of the melt will provide reduced inclusion sizes and distribution, improved surface finish and greatly improved fatigue life of DFT wire forms under various conditions pertinent for the medical-device industry.

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.

Drawn Filled Tube (DFT) is used in the pacing industry to provide a composite structure with ASTM F 562 material on the outer sheath and pure silver on the core. This material provides an excellent combination of properties: strength and corrosion resistance from the ASTM F 562, and good conductivity from the silver.

Figure 1 shows a cross section of DFT material at .102" Ø.

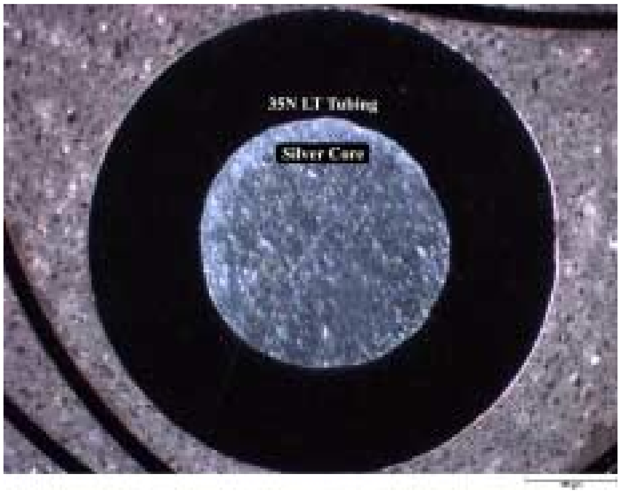

Figure 1. Cross section of DFT at .102" Ø.

Background

The principal high cycle fatigue failure mechanism in standard ASTM F 562 wire 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.

An improved process was developed which overcomes these limitations. This report describes the improvement in both microcleanliness 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 rolled and centerless ground to 1" ∅ bar. The bars were then gun drilled into tube hollows and reduced through drawing. The finished tubing was cleaned, filled with silver, and closed to 100% dense composite. 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 200 to 230 ksi.

Sample Preparation

Wires were produced to the .007 final diameter from three sets of DFT composites. One spool of 35N LT DFT was produced from the 35N LT alloy tubing. Two existing suppliers of the ASTM F 562 tubing were used to produce samples identified as ASTM F 562 Supplier A and Supplier B.

Testing

Microcleanliness Evaluation Procedure: An historical survey of eight (8) ASTM F 562 standard samples were cut at 0.102” ∅ hard drawn material. These samples represented five (5) melted master heats. Two (2) samples of 35N LT alloy were cut from 1” ∅ and 0.216” ∅ 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).

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. Rotary beam testing places the sample under cyclic, fully reversed tensile and compressive stresses. The high cycle rate of 3600 rpm produced 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 occurred when the wire broke. The testing equipment sensed the wire break and recorded 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, µm	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 2.

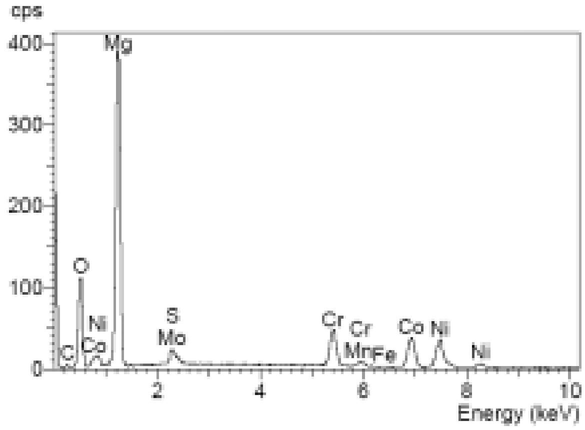

Figure 2. EDS spectra for dark inclusion in 35N LT Alloy

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.

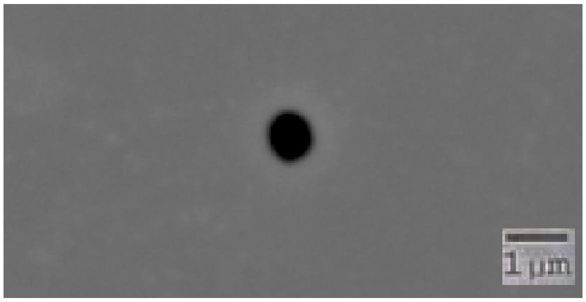

Image 1. BEI of a typical 35N LT Alloy inclusion feature.

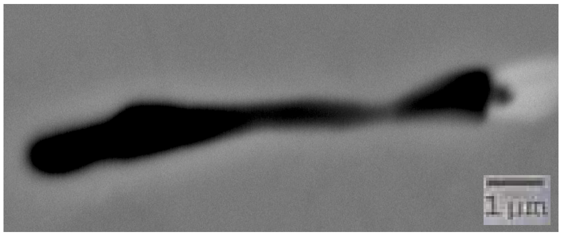

Image 2. BEI of largest inclusion feature in the 35N LT Alloy

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.

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

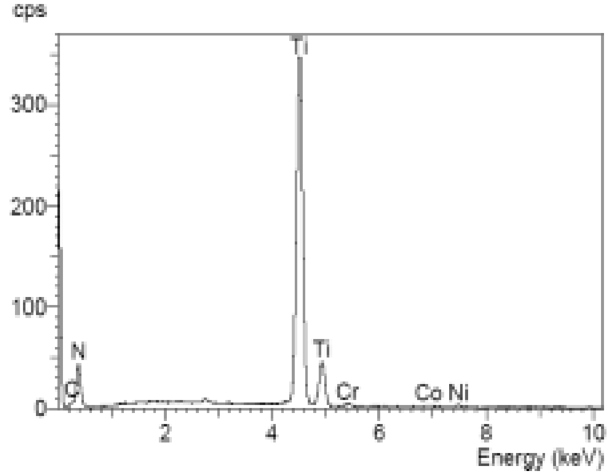

Figure 3. EDS spectra of darker inclusions in ASTM F 562 standard wire

Images 3 and 4 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.

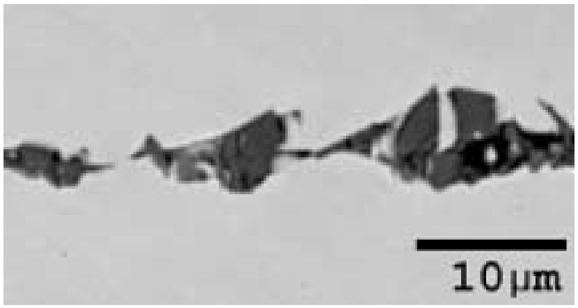

Image 3. BEI of typical over median size inclusion feature in standard ASTM F 562 material

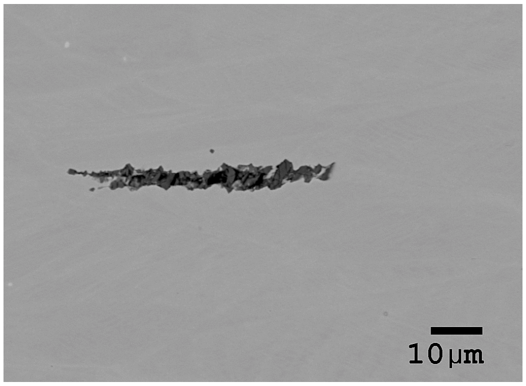

Image 4. BEI of the largest dark inclusion feature in ASTM F 562 material.

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

Table 2: Chemistry comparison of 35N LT DFT sheath to ASTM F 562

	ASTM F562		
Element	Min	Max	35N DFT
Carbon	-	0.025	0.006
Manganese	-	0.15	0.01
Silicon	-	0.15	0.01
Phosphorus	-	0.015	0.003
Sulfur	-	0.01	0.0001
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

Mechanical Properties

Tension Testing: Tensile properties of standard ASTM F 562 alloy DFT wire and 35N LT alloy DFT wire are comparable, as seen in Table 3. Test results were obtained using 200 lb. load cell, 10 inch gage length, and a 5 inch/minute cross head speed on an Instron model 4469 system.

Table 3. Summary of tension testing results.

Process Type	35N LT DFT	ASTM F 562 DFT Supplier A	ASTM F 562 DFT Supplier B
Diameter, in.	0.00706	0.00706	0.00702
UTS, Ksi	218	218	221
YS, Ksi	199	196	187
Elong, %	2.3	2.7	2.8

Fatigue Testing: Positool 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 4.

Table 4. The average number of cycles to failure.

Stress Value	35N LT DFT	ASTM F 562 DFT Supplier A	ASTM F 562 DFT Supplier B
250 Ksi	15,341	10,214	10,147
200 Ksi	41,811	21,595	20,273
150 Ksi	162,185	50,333	50,688
125 Ksi	15,069,240	104,462	94,531
110 Ksi	29,110,623	220,351	229,644
100 Ksi	46,538,769	299,695	1,096,200

Beginning with the highest tested stress level of 250 ksi, the improvement achieved by the 35N LT DFT is evident. The improvement continues and is most dramatic nearer the actual in-use range of 100 ksi. Figure 4 illustrates these data arranged in the typical S-N curve format.

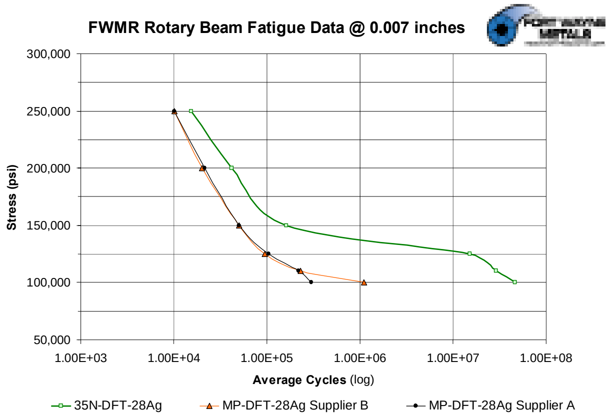

Figure 4. S-N Plot of Data Presented in Table 4.

Weibull Analysis

Weibull analysis is the leading method in the world for fitting and analyzing life data[1]. The primary advantage of the Weibull analysis is the ability to provide reasonably accurate failure analysis and failure forecasts with extremely small samples. Small samples also allow cost effective component testing. Another advantage of the Weibull analysis is that it provides a simple and useful graphical plot. The horizontal scale is a measure of life or aging [cycles to failure]. The vertical scale is the Cumulative Distribution Function (CDF) or cumulative percentage failed. It describes the percentage that will fail at any age.

The two defining parameters of the Weibull plot are the slope or shape parameter, Beta – β, and the characteristic life or scale parameter; Eta, - η. The Beta value indicates the class of failure mode such as infant mortality, random, or wear out. The eta value is the age at which 63.2% of the units will fail.

The coefficient of determination value, r^2, is a measure of the goodness of fit for the plot. The coefficient of determination is equal to the percentage of the variation in the data that is explained by the fit to the distribution. A perfect fit would be a value of 1.0.

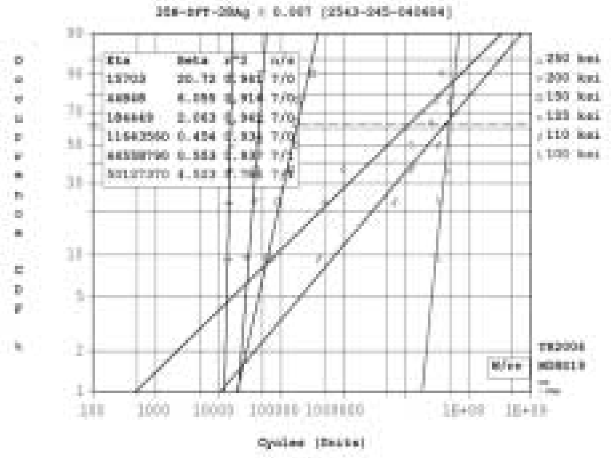

Figure 5 35N LT DFT Weibull Plot of data in Table 4.

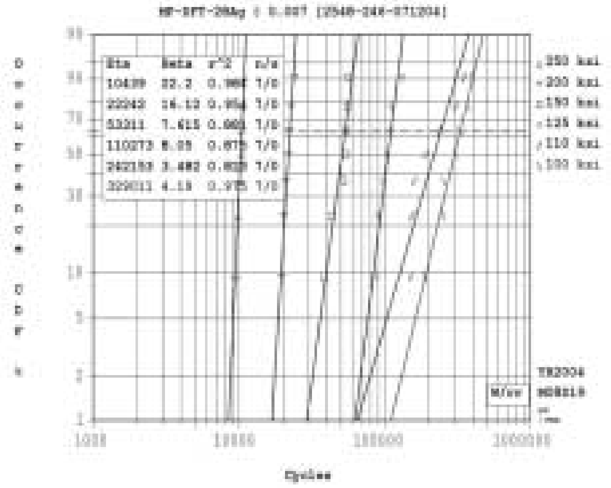

Figure 6. Weibull Plot of ASTM DFT Supplier A material of data in Table 4.

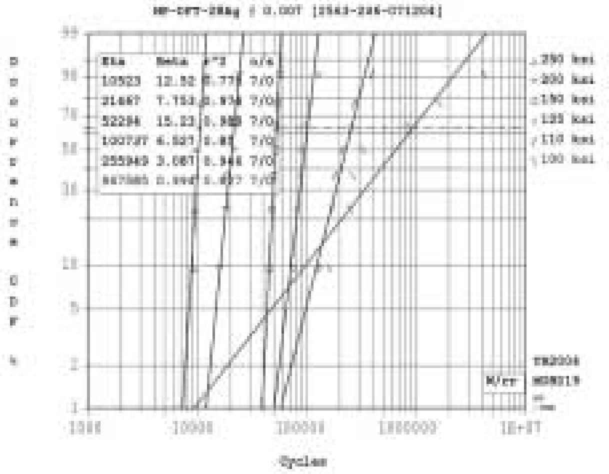

Figure 7. Weibull Plot of ASTM DFT Supplier B material of data in Table 4.

Table 5 Summary of Weibull Statistics

Process Type	Eta	Beta	r^2	n/s
ASTM F 562 Supplier A	329,011	4.19	0.975	7/0
ASTM F 562 Supplier B	947,585	0.994	0.827	7/0
35N LT DFT	50,127,370	4.523	0.784	7/4

These statistics indicate a significant improvement in the critical statistics of the Weibull analysis. The B62.3 value for the 35N LT DFT is 519% improvement over the standard ASTM F 562 DFT.

Conclusion

An optimized process has been developed that results in improved microcleanliness and greatly increased fatigue life in the new 35N LT DFT wire when compared with the standard ASTM F 562 DFT wire.

The goal of fatigue testing is to establish the endurance limit of the material[1, 2]. 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. The most significant conclusion regarding the fatigue testing of the new 35N LT DFT is the establishment of an endurance limit much greater than the existing ASTM F 562 DFT 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 relatively large TiN inclusions in standard ASTM F 562 material are not conducive to the use of the material in ultra fine diameter coil designs. As devices trend towards smaller lead designs, the availability of 35N LT DFT may allow such designs to evolve from standard ASTM F 562 DFT to improved 35N LT DFT with increased safety margins with respect to fatigue failure.

The test results confirm the improvement in average fatigue life of this new alloy system by at least 4145% at the 100 ksi stress level.

References

1. Abernathy, Dr. Robert B., The New Weibull Handbook, 2000
2. Fehring, Thomas K., et al., U.S. Patent No. 6,187,045, “Enhanced biocompatible implants and alloys, February 13, 2001.
3. Fehring, Thomas K., et al., U.S. Patent No. 6,539,607 B1, “Enhanced biocompatible implants and alloys, April 1, 2001.

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