

The Implementation of a Second Source for Electron Beam Refined Nitinol (HCF-SE) using Fort-Wayne-Metals Vacuum-Arc-Remelted Ingots

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Introduction

In the medical device industry Nitinol is a main material for various applications like stents and heart valve frames that are made from Nitinol tubing. The number of Nitinol ingot suppliers is limited, and Fort Wayne Metals (FWM) extended their melting capacity to supply Nitinol bar for tube manufacturing.

Consequently, the cooperative project PRIME (PRoficient Ingot Material Evaluation) was started driven by a collective of industry leaders along the process chain. The collective consists of the melt supplier Fort Wayne Metals, continuing along the process chain with Nitinol tube manufacturers Vascotube and Euroflex and finally medical device contract manufacturers MeKo and Admedes. This collaborative project is dedicated to evaluate the new Nitinol source for tube processability and device manufacturing requirements.

The project includes different melting methods resulting in different material grades as well as different tube sizes. This part of the white paper focuses on so called Gen III Material. Generation I Nitinol Vacuum Arc Remelt (VAR) ingot material is used as a base material for Electron Beam Refinement (EBR) resulting in Generation III material, known as HCF-SE. Euroflex and Vascotube processed HCF-SE into tubes and Admedes and MeKo manufactured components.

Keywords: Nitinol, VAR, EBR, Tube, Component

1 VAR-EBR INGOT

At G.Rau GmbH several VAR ingots were refined using FWM ASTM F2063 conform pre-material ingots. Heat 337464 and heat 12281 were used for the following investigations that met the full requirements of ASTM F2063. A summary of the chemical requirements and analysis is shown in Table 1.

Element in % (mass/ mass)	ASTM F2063	337464	12281
Ni	54.5 to 57.0	55.3	55.65
C, max.	0.040	0.001	0.003
Co, max.	0.050	0.004	0.0012
Cu, max.	0.010	0.0017	0.0027
Cr, max.	0.010	0.0033	0.0011
H, max.	0.005	0.0009	0.001
Fe, max.	0.050	0.018	0.013
Nb, max.	0.025	0.002	0.002
N, max.	0.005	0.003	0.0005
O, max.	0.040	0.021	0.019

Table 1: Chemical composition requirements and analysis.

Figure 1 is one differential scanning calorimetry (DSC) curve of heat 337464 in fully annealed condition. The corresponding Austenitic start (As) transformation temperature is -28 °C and Austenitic finish (Af) temperature is -15 °C. The As transformation temperature range requirement of ASTM F2063 specifying a maximum range of 20 °C is fulfilled. In Table 2 transformation temperatures of both heats are listed.

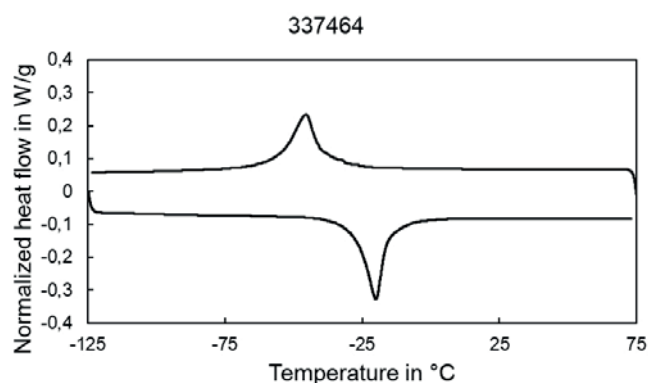


Fig. 1: Differential scanning calorimetry of fully annealed heat 337464.

Heat	As in °C	Af in °C
337464	-28	-15
12281	-30	-17

Table 2: Ingot As and Af temperatures.

Figure 2 is a representative micrograph of HCF mill product in annealed condition showing the inclusion size satisfied the ASTM F2063 requirements and HCF-SE specification (see Table 2). In addition, the ASTM grain size number 9 of the mill product fulfilled ASTM F2063 requirement of ASTM grain size number 4 or finer.

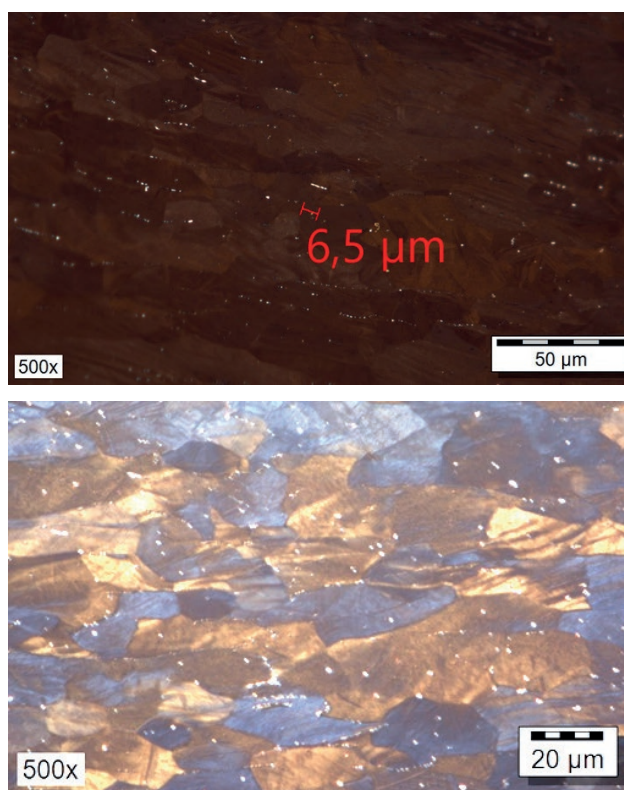


Fig. 2: Micrograph of mill product (337464) for inclusion (upper) and grain size analysis (lower).

	VAR-EBR specification	337464	12281
Max. inclusion	10 µm	8.3 µm	8.5 µm
Max. area fraction	0.7 %	0.5 %	0.6 %

Table 3: Inclusion size and area fraction of VAR-EBR ingots.

2 TUBE MANUFACTURING

Three different tube sizes were manufactured by Euroflex (outer diameter 7 mm and wall thickness 0.5 mm, outer diameter 4 mm and wall thickness 0.1 mm, outer diameter 2.18 mm and wall thickness 0.35 mm) and one tube size by Vascotube (outer diameter 2.18 mm and wall thickness 0.35 mm) according to standard specifications (see Table 4). Each manufactured tube batch was shipped to medical device contract manufacturers Admedes and MeKo. Both medical device contract manufacturers conducted incoming inspection by examining the microstructure and mechanical properties on the incoming tube from each batch.

Tube sizes	7.00 mm x 0.50 mm, 4.00 mm x 0.10 mm and 2.18 mm x 0.35 mm
UTS min.	1100 MPa
UPS min. (at 3%)	380 MPa
Elongation at fracture min.	12 %
Max. residual elongation after 6 %	0.3 %
Af max.	15 °C

Table 4: Tube specifications

Tube (mm)		Admedes	MeKo
7.00 x 0.50	Max. inclusion	3 µm	5 µm
	Area fraction	0.26 %	0.09 %
4.00 x 0.10	Max. inclusion	3 µm	2 µm
	Area fraction	0.50 %	0.01 %
2.18 x 0.35 (Euroflex)	Max. inclusion	3 µm	4 µm
	Area fraction	0.68 %	0.40 %
2.18 x 0.35 (Vascotube)	Max. inclusion	3 µm	3.5 µm
	Area fraction	0.64 %	0.14 %

Table 5: Max. inclusion size and area fraction of VAR-EBR tubing.

Figure 3 and Figure 4 show the microstructure of the finished tubing in the longitudinal direction. The maximum inclusion size and area fraction are listed in Table 5. The focus of this analysis was to understand if stringers were formed during the tube manufacturing process as a consequence of cold forming steps. No stringers and voids were observed at 500x magnification.

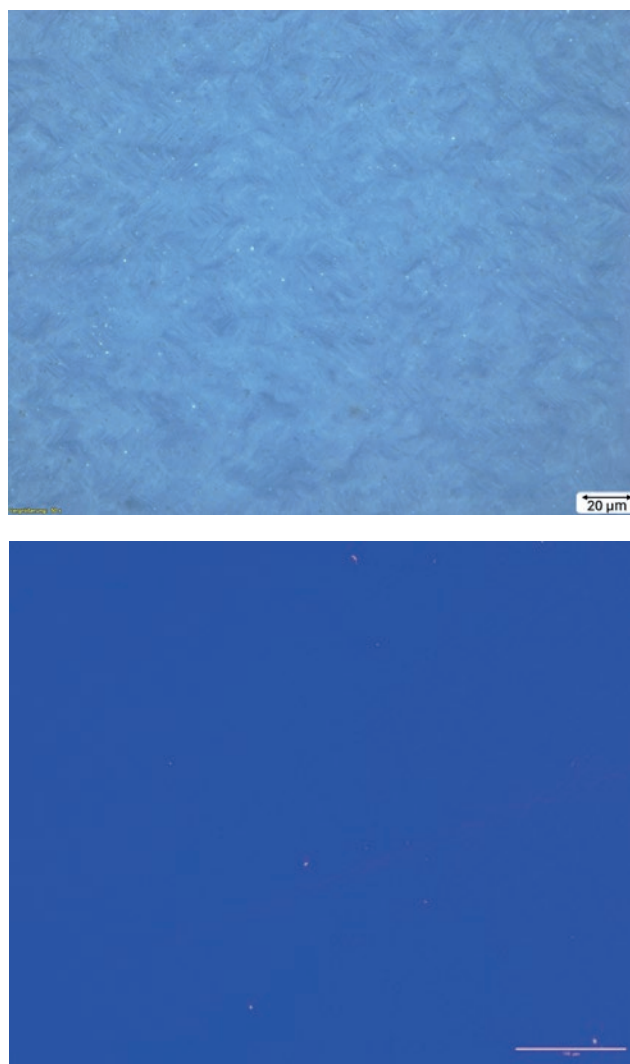


Fig. 3: Inclusion analysis of 7 mm x 0.5 mm tube in longitudinal direction using 500x magnification. Upper: Analysis by Admedes. Lower: Analysis by MeKo.



Fig. 4: Inclusion analysis of 4 mm x 0.1 mm tube in longitudinal direction using 500x magnification. Upper: Analysis by Admedes. Lower: Analysis by MeKo.

Admedes and MeKo used a dogbone-shaped geometry (see Figure 5) to perform mechanical testing of tubes according to ASTM F2516. Admedes ran the tests at room temperature (22 °C) and MeKo at body temperature (37 °C). Resulting tensile test diagrams for 7 mm x 0.5 mm tubing are shown in Figure 6 and for 4 mm x 0.1 mm tubing in Figure 7. A summary of mean mechanical properties including results from Euroflex and Vascotube are listed in Table 6. In contrast to the dogbone sample geometry having a 0.5 mm thin strut width, Euroflex and Vascotube tested full circumference tube samples. Each company used its own test conditions. The differences observed align with the expectations.

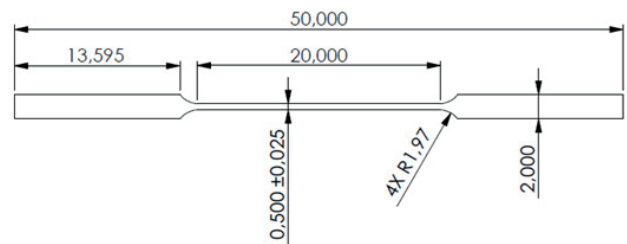


Fig. 5: Geometry of dogbone used for tension testing

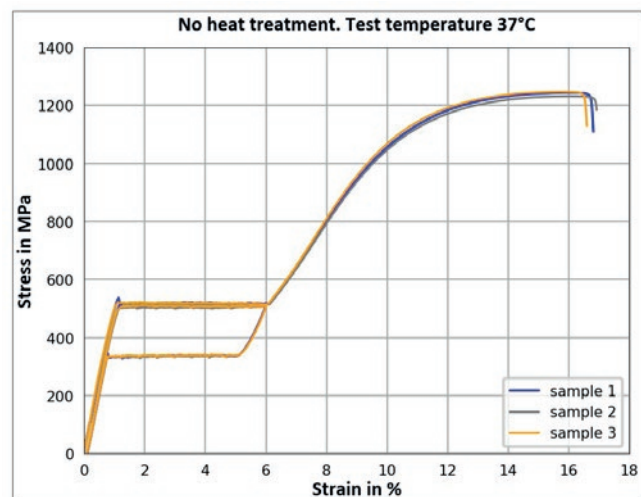
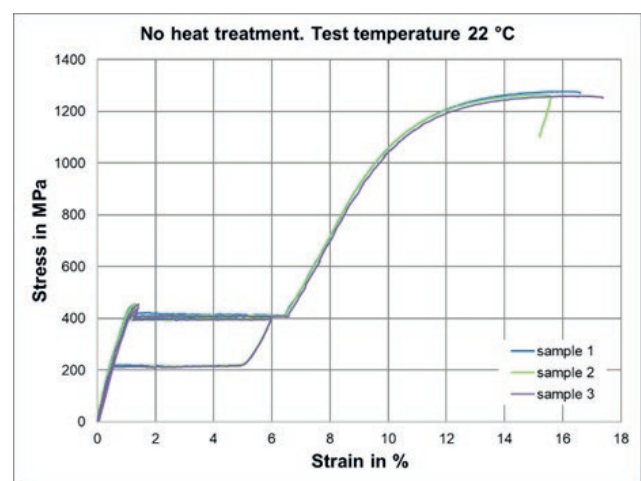


Fig. 6: Tensile test results 7x0.5 mm tube. Upper: Admedes at 22 °C. Lower: MeKo at 37 °C.

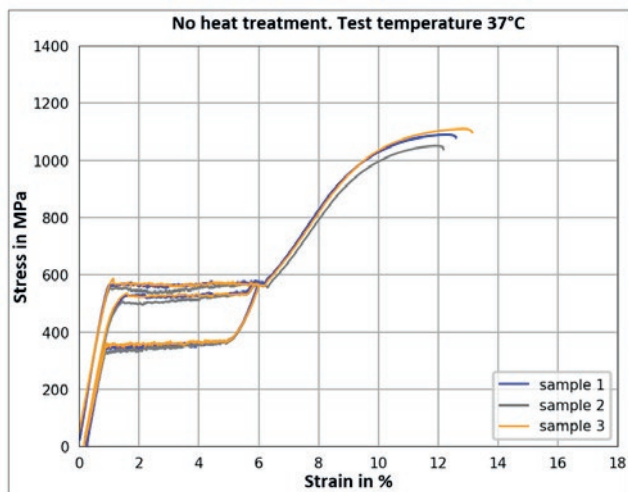
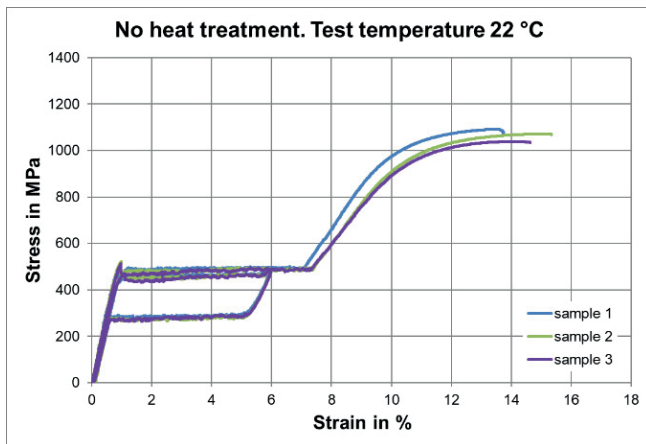


Fig. 7: Tensile test results 4 mm x 0.1 mm tube. Upper: Admedes at 22 °C. Lower: MeKo at 37 °C.

The transformation temperature was measured using the so-called crush method. It is based on ASTM F2082. A tube section approximately 5 mm long was cooled down in an alcohol bath to -55 °C, the section was crushed into an oval but did not exceed 3 % strain. The bath was heated up to 20 °C with 5 ° C/min. The Af was determined using the same tangent line method as described in ASTM F2082. The results are listed in Table 7 and are within the tube specifications.

Mech. Properties	UTS in MPa	UPS in MPa	LPS in MPa	Ef in %
7.00 mm x 0.50 mm tube				
Admedes 22 °C	1266	412	214	16.4
MeKo 37 °C	1241	517	336	16.8
Euroflex 22 °C	1234	446	194	23.2
4.00 mm x 0.10 mm tube				
Admedes 22 °C	1067	479	279	14.6
MeKo 37 °C	1083	557	353	12.6
Euroflex 22 °C	1134	491	261	22.8
2.18 mm x 0.35 mm tube Euroflex				
Admedes 22 °C	1254	493	287	13.4
MeKo 37 °C	1213	559	327	17.0
Euroflex 22 °C	1245	492	266	22.1
2.18 mm x 0.35 mm tube Vascotube				
Admedes 22 °C	1220	420	196	15.8
MeKo 37 °C	1131	462	259	15.5
Vascotube 22 °C	1212	426	168	16.9

Table 6: Average tube mechanical properties.

Tube Size	Admedes	MeKo
7.00 mm x 0.50 mm	-7.3 °C	-7.4 °C
4.00 mm x 0.10 mm	-20.4 °C	-20.0 °C
2.18 mm x 0.35 mm (Euroflex)	-8.2 °C	-9.0 °C
2.18 mm x 0.35 mm (Vascotube)	-0.9 °C	-0.9 °C

Table 7: Af temperature of tubes.

3 COMPONENT MANUFACTURING

Admedes and MeKo used the HCF-SE Nitinol tubing to evaluate the material in the component manufacturing process chain by producing generic heart valve frames, neuro stents and peripheral stents. For the generic heart valve frames shown in Figure 8 the tube size of 7 mm x 0.5 mm was used, for the neuro stents shown in Figure 9 the tube size of 4 mm x 0.1 mm and for the peripheral stents in Figure 10 the tube size of 2.18 mm x 0.35 mm. Both manufacturers used their standard process chains including laser cutting, heat treatment, and surface removal processes.

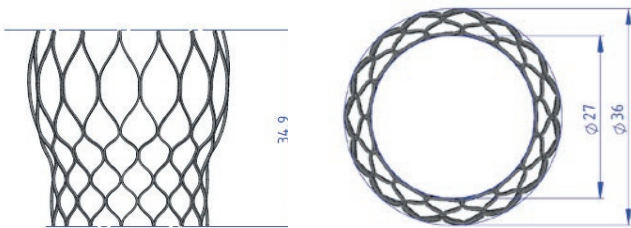


Fig. 8: Generic heart valve frame design in front and top view

In total, MeKo and Admedes manufactured 44 heart valve frames. At both contract manufacturers there were no complications during laser cutting, heat treatment, or surface processes.

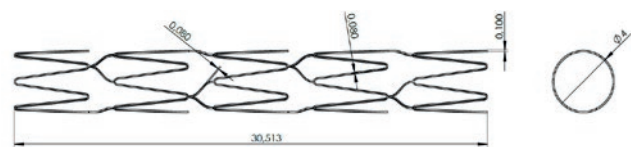


Fig. 9: Neuro stents frame design in front and top view

In addition, 40 generic neuro stents were manufactured. Both device contract manufacturers observe high scrap rates due to varying geometry like inconstant strut width. The higher scrap rate can be attributed to high residual stresses in the Nitinol tube due to a high diameter-wall thickness-ratio and is not heat related. Moreover, 92 peripheral stents were fabricated. There were no deviations observed throughout the process chain.

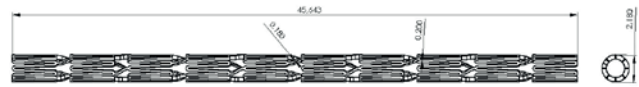


Fig. 10: Unexpanded peripheral stent.

3.1 Surface

The surface of the heart valve frames, neuro stents and peripheral stents were inspected by light microscope and scanning electron microscope (SEM).

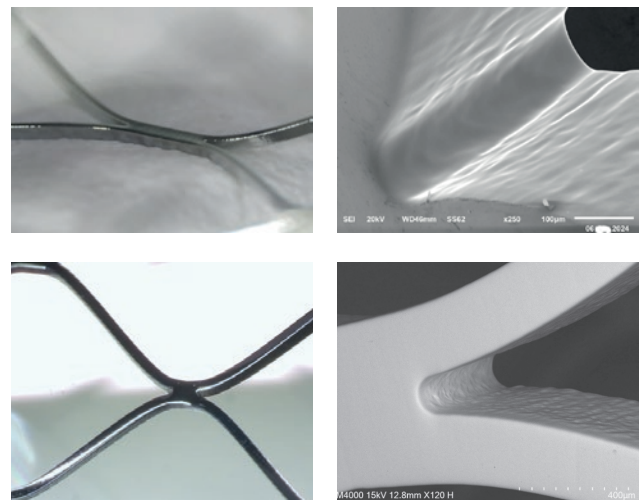


Fig. 11: Light microscope (left) and SEM (right) of heart valve frames. Upper: Admedes. Lower: MeKo.

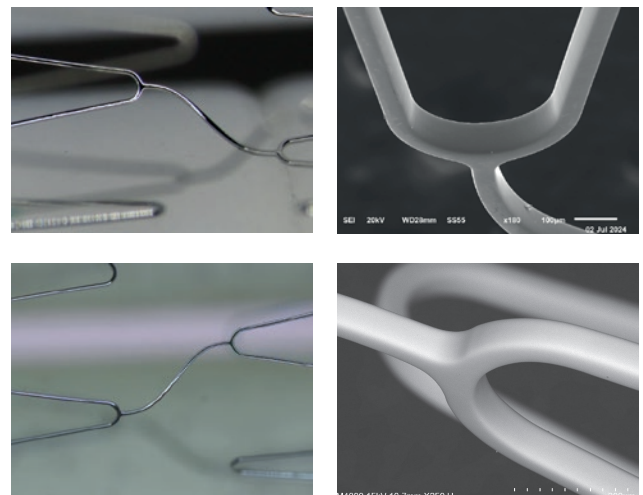


Fig.12: Light microscope (left) and SEM (right) of neuro stents. Upper: Admedes. Lower: MeKo.

Representative pictures of the heart valve frames of the outer diameter, inner diameter, and tip ends are shown in Figure 11. Representative pictures of the generic neuro stent design and peripheral stents are shown in Figure 12 and Figure 13. In summary, there were no material related defects observed at either contract manufacturer.

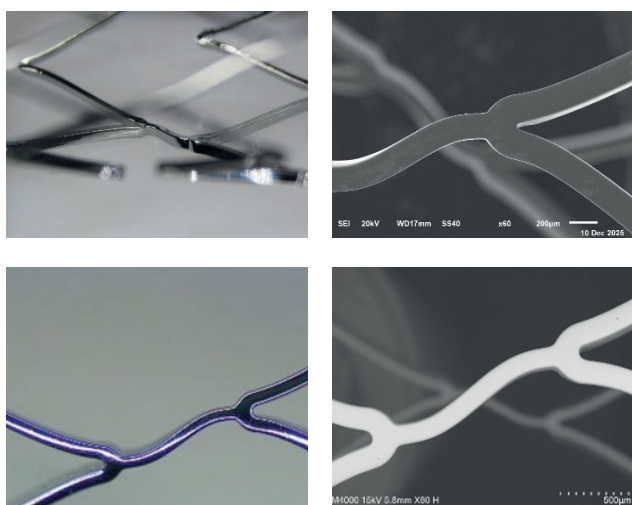


Fig. 13: Light microscope (left) and SEM (right) of peripheral stents made from Vascotube tube. Upper: Admedes. Lower: MeKo.

4 DIFFERENTIAL SCANNING CALORIMETRY

DSC tests of the heat-treated components were conducted based on ASTM standard F2004. Each contract manufacturer used their standard temperature range for DSC. For MeKo the range is between -80 °C and 60 °C and for Admedes between -180 °C and 100 °C.

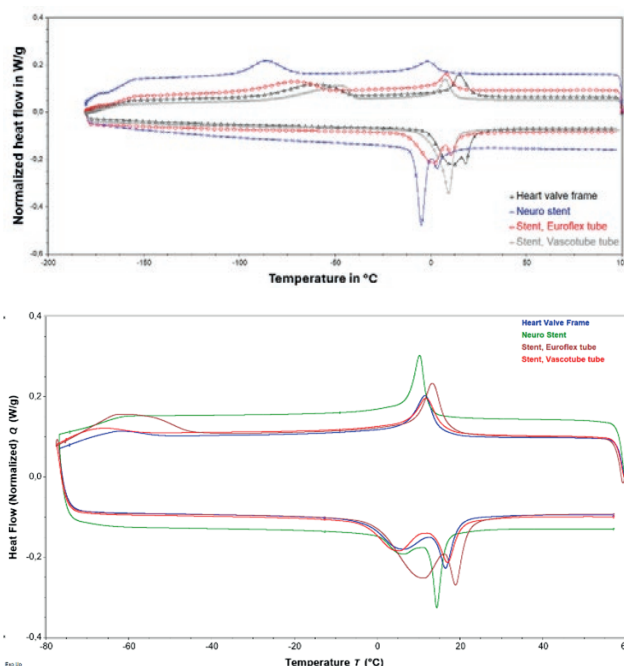


Fig. 14: DSC curves of heart valve frame, neuro stents and stents after heat treatment by Admedes (upper) and MeKo (lower).

The contract manufacturers chose expansion and heat treatment steps independently of each other. The DSC results are shown in Figure 14 and fulfilled the expectations.

5 RADIAL FORCE

The heart valve frames with an outer diameter of 36 mm were crimped in three crimp cycles to a decreasing crimp diameter of 25 mm, 20 mm and 7 mm to determine the radial force. The results are shown in Figure 15. The test results of MeKo (see Figure 15 lower) show a maximum diameter of 30 mm as it is the maximum diameter of the radial force tester. The results met the expectations.

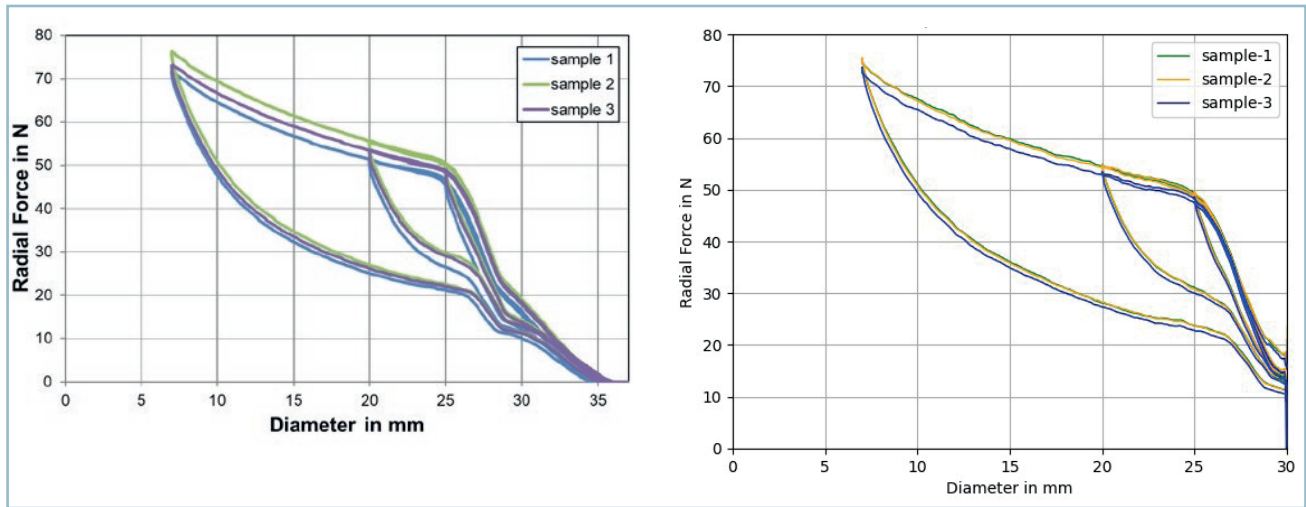


Fig. 15: Radial force tests of heart valve frames by Admedes (left) and MeKo (right).

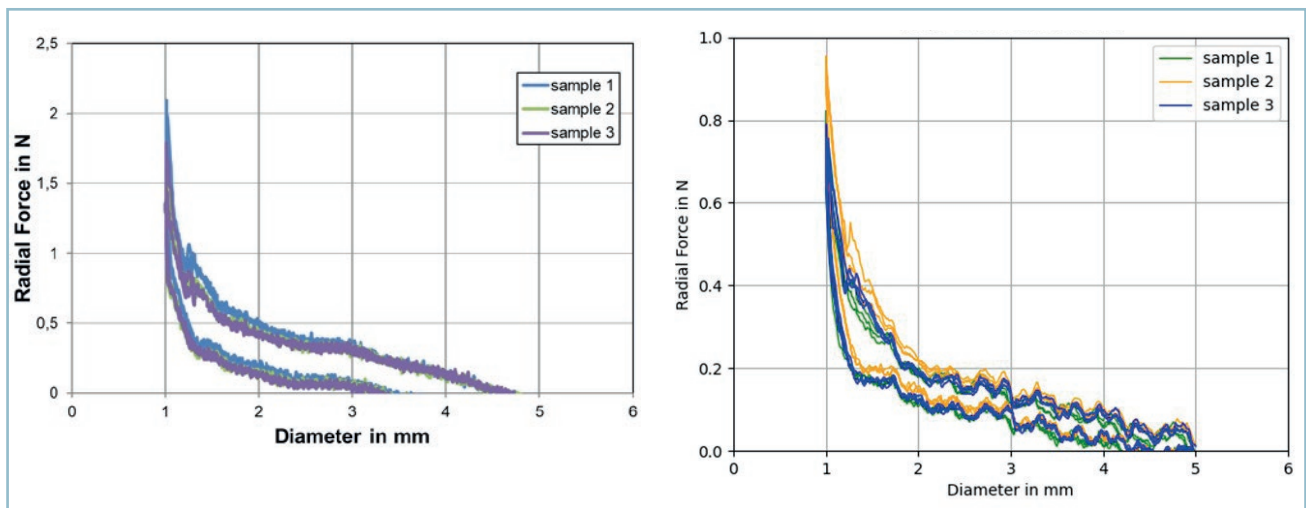


Fig. 16: Radial force tests of neuro stents by Admedes (left) and MeKo (right).

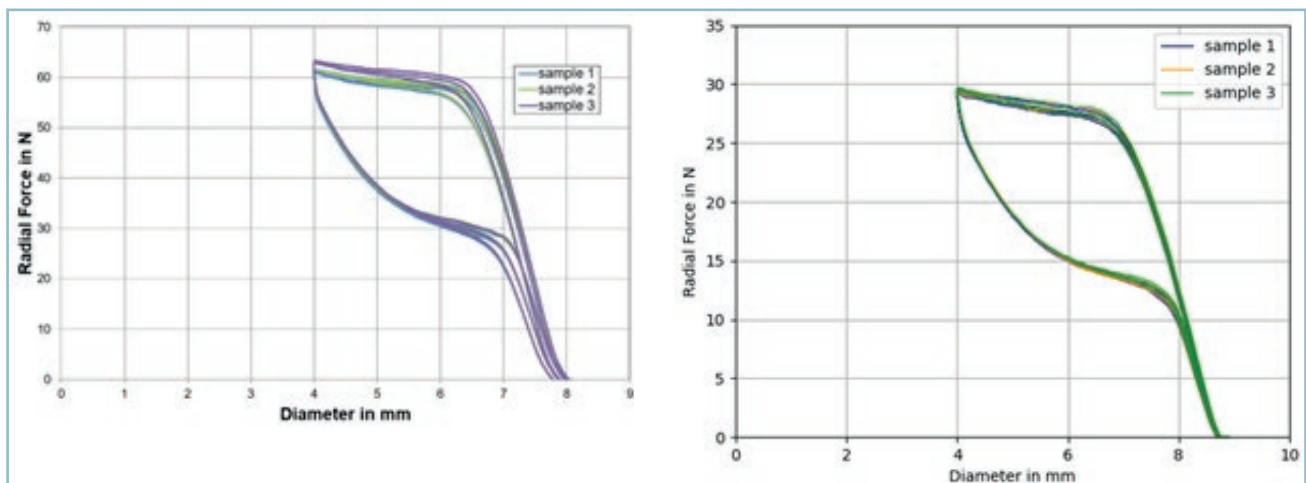


Fig. 17: Radial force tests of peripheral stents of Vascotube tube tested by Admedes (left) and MeKo (right).

The neuro stents with a diameter of 4.3 mm were crimped in three crimp cycles to a crimped diameter of 1 mm, see Figure 16. The peripheral stents were crimped to a diameter of 4 mm, see Figure 17. There were three crimping repetitions conducted, the same number of cycles like the other samples. Due to the differences

in Af temperature and strut width, the radial force results align with the anticipated outcomes.

6 CORROSION

No.	Sample	Er in mV (SCE)	Eb in mV (SCE)	Ev in mV
1	HVF	-238	nB	1000
2	HVF	-402	nB	1000
3	HVF	-401	nB	1000
4	HVF	-375	nB	1000
5	HVF	-389	nB	1000
6	HVF	-231	nB	1000
7	HVF	-408	nB	1000
8	HVF	-433	nB	1000
9	HVF	-389	nB	1000
10	HVF	-434	nB	1000
1	Neuro stent	-352	nB	1000
2	Neuro stent	-329	nB	1000
3	Neuro stent	-264	nB	1000
4	Neuro stent	-259	nB	1000
5	Neuro stent	-267	nB	1000
1	Stent Euroflex	-406	nB	1000
2	Stent Euroflex	-401	nB	1000
3	Stent Euroflex	-418	nB	1000
4	Stent Euroflex	-425	nB	1000
5	Stent Euroflex	-406	nB	1000
1	Stent Vascotube	-353	nB	1000
2	Stent Vascotube	-464	nB	1000
3	Stent Vascotube	-102	nB	1000
4	Stent Vascotube	-317	nB	1000
5	Stent Vascotube	-75	nB	1000

Table 8: Corrosion test results of heart valve frames, neuro and peripheral stents by Admedes.

The samples were subjected to corrosion testing using cyclic potentiodynamic polarization in phosphate-buffered saline solution at body temperature according to ASTM F2129. A saturated calomel electrode (SCE) was used as the reference electrode. Admedes and MeKo tested at least 5 samples from every tube lot.

The results of heart valve frames (HVF), neuro and peripheral stents are summarized in Table 8 and Table 9. There were either high breakdown potentials over 900 mV or no breakdown (nB) observed, meaning the parts were considered corrosion resistant.

No.	Sample	Er in mV (SCE)	Eb in mV (SCE)	Ev in mV
1	HVF	-401	977	1300
2	HVF	-399	957	1300
3	HVF	-356	962	1300
4	HVF	-276	996	1300
5	HVF	-329	1011	1300
1	Neuro stent	-361	950	1300
2	Neuro stent	-380	997	1300
3	Neuro stent	-407	994	1300
4	Neuro stent	-328	1018	1300
5	Neuro stent	-419	971	1300
1	Stent Euroflex	-415	956	1300
2	Stent Euroflex	-298	1013	1300
3	Stent Euroflex	-452	999	1300
4	Stent Euroflex	-413	1011	1300
5	Stent Euroflex	-375	1005	1300
1	Stent Vascotube	-431	1001	1300
2	Stent Vascotube	-427	1003	1300
3	Stent Vascotube	-418	998	1300
4	Stent Vascotube	-425	1008	1300
5	Stent Vascotube	-428	990	1300

Table 9: Corrosion test results of heart valve frames, neuro and peripheral stents by MeKo.

7 FATIGUE TESTS

To prove the material quality of the HCF-SE using FWM GEN I ingot, a diamond fatigue study was conducted. The tests were performed at G.RAU Inc. located in Scotts Valley, California.

Both component manufacturers produced a series of diamonds according to the drawing shown in Figure 18. The diamonds were expanded and heat treated using the same recipe.

For FEA purposes, dogbone specimens were produced using the same heat treatment parameters as for the diamond specimens to collect data for the FEA analysis. Tensile test results are shown in Figure 19. With FEA output it is possible to calculate the stress-strain relationship from the force-displacement data which was collected during the fatigue tests.

In addition, the dogbones were used to take DSC measurements to make sure that both series of specimens had the same transformation temperatures (see Table 10).

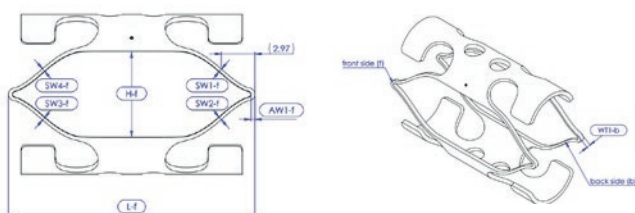


Fig. 18: Diamond fatigue specimen for 7 mm x 0.5 mm tubing.

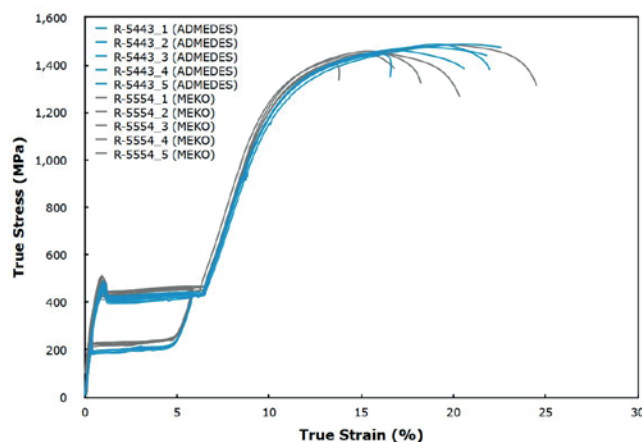


Fig. 19: Tensile test of heat treated dogbones to collect input parameters for FEA.

Nitinol Tensile Dogbone Lot 700019127 (R-5443_1)		Nitinol Tensile Dogbone Lot 700019127 (R-5443_2)		Nitinol Tensile Dogbone Lot 700019127 (R-5443_3)		Nitinol Tensile Dogbone Lot 700019127 (R-5443_4)		Nitinol Tensile Dogbone Lot 700019127 (R-5443_5)	
Transformation Step		Temperature (°C)		Temperature (°C)		Temperature (°C)		Temperature (°C)	
R _s		15.3		16.0		15.5		15.7	
R _p		11.5		11.9		11.3		11.6	
R _t		6.8		6.8		5.9		6.4	
M _s		-47.7		-47.8		-47.1		-47.6	
M _f		-66.7		-67.1		-67.0		-67.2	
M ₀		N/A		N/A		N/A		N/A	
R _s		-4.4		-3.6		-3.3		-3.3	
R _p		7.5		8.6		9.5		9.1	
A ₀		17.2		18.6		18.8		18.8	
A _v		21.0		22.5		22.8		22.7	
Transformation		Enthalpy (J/g)		Enthalpy (J/g)		Enthalpy (J/g)		Enthalpy (J/g)	
R		3.3		3.4		3.4		3.4	
M		N/A		N/A		N/A		N/A	
R/A		13.1		13.5		13.8		13.5	
Nitinol Tensile Dogbone Lot 700019127 (R-5443_1)		Nitinol Tensile Dogbone Lot 700019127 (R-5443_2)		Nitinol Tensile Dogbone Lot 700019127 (R-5443_3)		Nitinol Tensile Dogbone Lot 700019127 (R-5443_4)		Nitinol Tensile Dogbone Lot 700019127 (R-5443_5)	
Transformation Step		Temperature (°C)		Temperature (°C)		Temperature (°C)		Temperature (°C)	
R _s		15.3		16.0		15.5		15.7	
R _p		11.5		11.9		11.3		11.6	
R _t		6.8		6.8		5.9		6.4	
M _s		-47.7		-47.8		-47.1		-47.6	
M _f		-66.7		-67.1		-67.0		-67.2	
M ₀		N/A		N/A		N/A		N/A	
R _s		-4.4		-3.6		-3.3		-3.3	
R _p		7.5		8.6		9.5		9.1	
A ₀		17.2		18.6		18.8		18.8	
A _v		21.0		22.5		22.8		22.7	
Transformation		Enthalpy (J/g)		Enthalpy (J/g)		Enthalpy (J/g)		Enthalpy (J/g)	
R		3.3		3.4		3.4		3.4	
M		N/A		N/A		N/A		N/A	
R/A		13.1		13.5		13.8		13.5	

Table 10: DSC Tests of heat-treated dogbones to show equivalency of both sets of diamonds. Upper: Admedes. Lower: MeKo.

Test Conditions	
Pre-Strain	9 %
Mean Strain	3 % and 5 %
Strain Amplitude	2.0 % and 3.0 %
Test Temperature	37 °C
Test Frequency up to 1000 cycles	1 Hz
Test Frequency up to 10 Mio cycles	25 Hz
Test Specimens per condition per component manufacturer	5

Table 11: Test conditions fatigue setup.

There were zero fractures observed under the 2 % strain amplitude-test conditions listed in Table 11. This result is in line with the reported tests using another VAR material supplier as pre-material for the HCF-SE refining process. Since this test was designed for test to fracture, the 3 % strain amplitude condition was added. All specimens had at least one fracture after 10 million cycles. Figure 20 also shows the current fatigue strain limit line for Gen I as a comparison. This means that the fatigue strain limit of HCF-SE was about 4 to 5 times higher than Gen I Nitinol material.

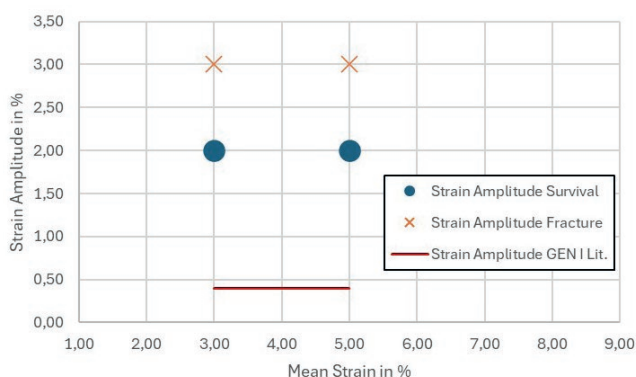


Fig. 20: Fatigue results diamond testing till 10 million cycles.

8 CONCLUSION

Within the context of the PRIME project Gen I Nitinol was supplied by Fort Wayne Metals and further processed using EBR by G. Rau GmbH. The objective was to verify whether the material functions effectively in the processes of each company along the process chain and whether the resulting products meet the quality requirements. Multiple Nitinol HCF-SE tube sizes were manufactured by Euroflex and Vascotube. In this white paper tubes with an outer diameter of 7 mm and wall thickness of 0.5 mm, an outer diameter of 4 mm and wall thickness of 0.1 mm, as well as an outer diameter of 2.18 mm and wall thickness of 0.35 mm were investigated and further processed to heart valve frames, neuro stents and peripheral stents.

The material investigation began with the melt, which complied with the relevant standard ASTM F2063 and Euroflex internal specifications. The produced bar machinability allowed gun drilling and subsequent fabrication into tubes. No complications were observed during tube drawing process of HCF-SE tube by Euroflex or Vascotube. The manufactured tubes met all specified mechanical and dimensional requirements. Furthermore, these tubes have been determined to serve as suitable semi-finished products for device manufacturing, with all analyzed results aligning with the expected quality and performance criteria. Specifically, the results of DSC, radial force, and corrosion tests were inconspicuous, and the surface quality met all quality requirements.

The fatigue specimens were manufactured from two different 7 mm x 0.5 mm tube lots. There were 10 total specimens tested per condition, 5 from each component manufacturer, with 5 specimens tested under the same condition. Therefore, one datapoint in Figure 20 represents 10 test results from fatigue specimens. Each diamond had eight critical fracture locations. This means that each datapoint represents 80 positions within the material.

Based on the results compiled in this paper, the FWM VAR-material which met ASTM F2063 requirements, is deemed suitable as a base material to make HCF-SE Gen III ingot. The final product made from those ingots shows the same performance regarding producibility, material characteristics and fatigue resistance as the currently used VAR base material.

With having two independent sources for VAR pre-material, the EBR process used to make HCF-SE decouples component manufacturers and their clients from instabilities in the ingot supply chain.



9 ACKNOWLEDGMENTS

The investigations discussed in this paper were funded by the partners Fort Wayne Metals Research Products, Vascotube a Cirtec Company, Euroflex GmbH, G.RAU GmbH & Co KG, Admedes GmbH and MeKo Manufacturing e.K..

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