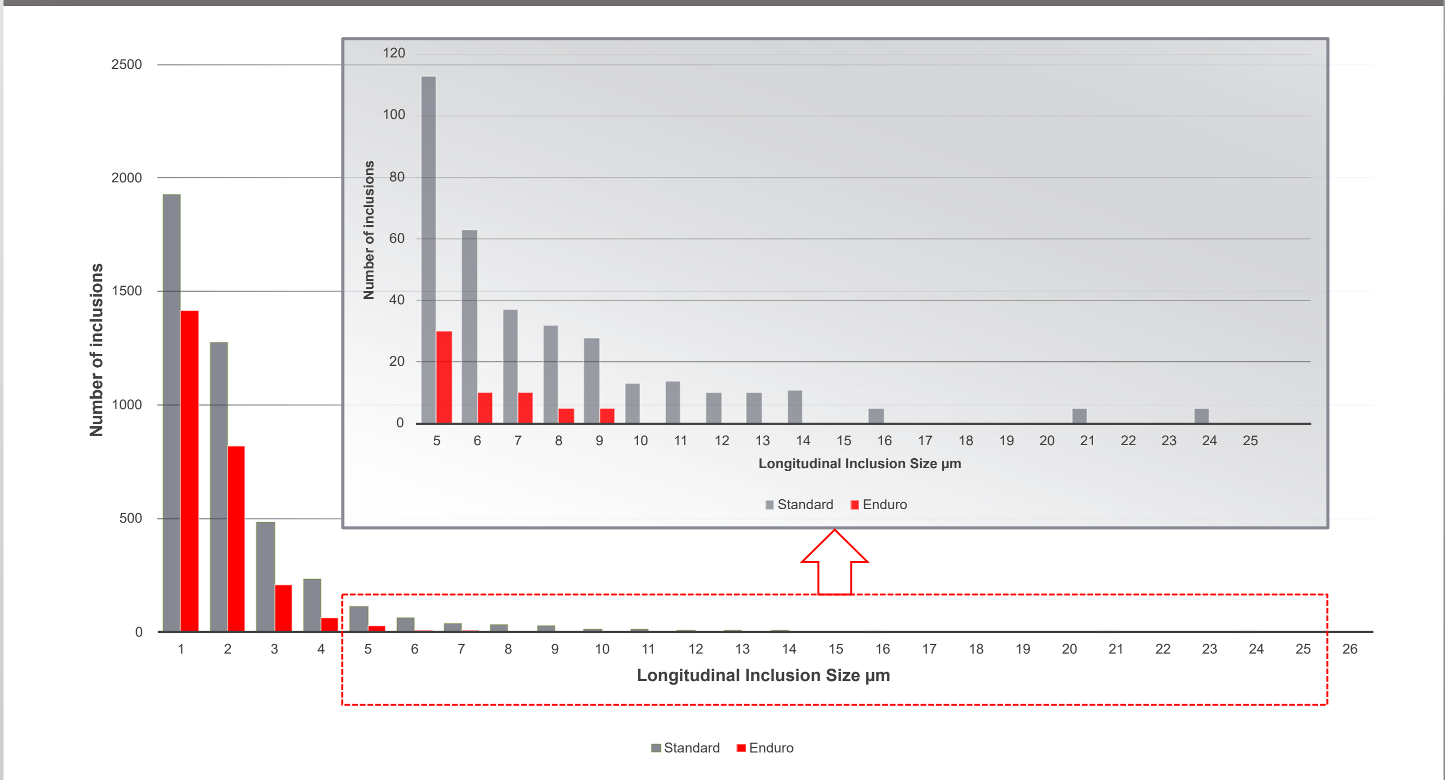
Enduro

A new nitinol material, engineered to go the distance in ultra-demanding applications.

- Significant reduction in inclusion size and area fraction, maximum 12.0 micron and 0.5% area fraction
- Drastic elimination of large carbides and oxides seen in commercial nitinol products
- Reduced inclusions throughout material cross section, not only the surface layer
- Enhanced fatigue life driven by material cleanliness and steep reduction of large inclusions
- ASTM F2063-18 compliant
- Available in commercial scale for components, tubes, wires, sheets and mill products
- Standard lead times

	Max inclusion size (µm)	Max inclusion area
ASTM F2063-18	39.0	2.8%
Standard	26.0	2.0%
Redox	20.0	1.2%
Enduro	12.0	0.5%

Inclusion distribution comparison of typical VIM-VAR and Enduro heats shows a dramatic decrease in large inclusions, resulting in significantly improved fatigue life



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SAES Smart Materials, Inc.
a SAES Group company

memry
a SAES Group company
nitinol+

Fatigue Testing of a New Generation of Commercial Scale Ultra-low Inclusion NiTi Alloy

May 17, 2022

Dr. Andie Pequegnat

saes group

memry™
a SAES Group company

nitinol +™

Enduro

Objectives

1. Characterize Nitinol wire material produced from SAES Smart Material (SSM) ultra-low inclusion Enduro ingot and benchmark with SSM's standard ingot
2. Demonstrate improved fatigue performance of the new Enduro Nitinol alloy

Agenda

- Background on Gen III Nitinol and Fatigue
- Experimental Sample Prep.
- Material Characterization
- RBT Fatigue Testing and Results
- Z-Specimen Testing and Results
- Summary

Enduro

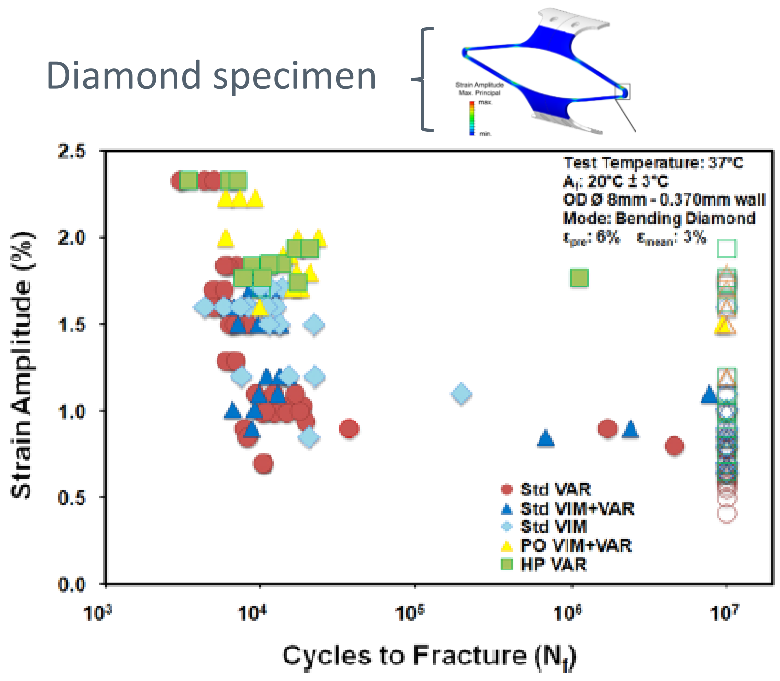
A new nitinol material, engineered to go the distance in ultra-demanding applications.

Background

Why low-inclusion Nitinol?

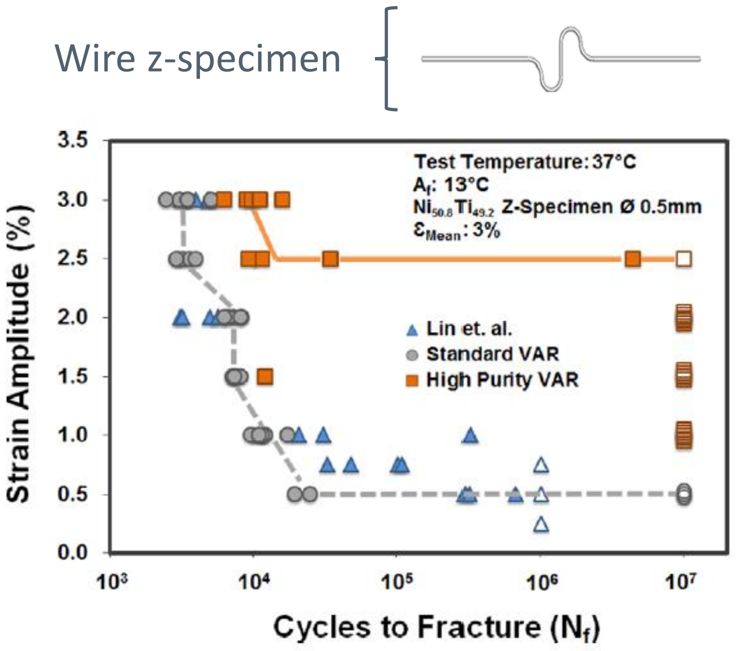
- Extensive studies conducted on the significant impact of inclusion size and density on fatigue
- Ultra-clean Nitinol materials becoming a requirement for cardiovascular and neurovascular implant applications that demand extreme durability

Diamond specimen



[S.W. Robertson et al., JMBBM, 51 (2015), p 119-131]

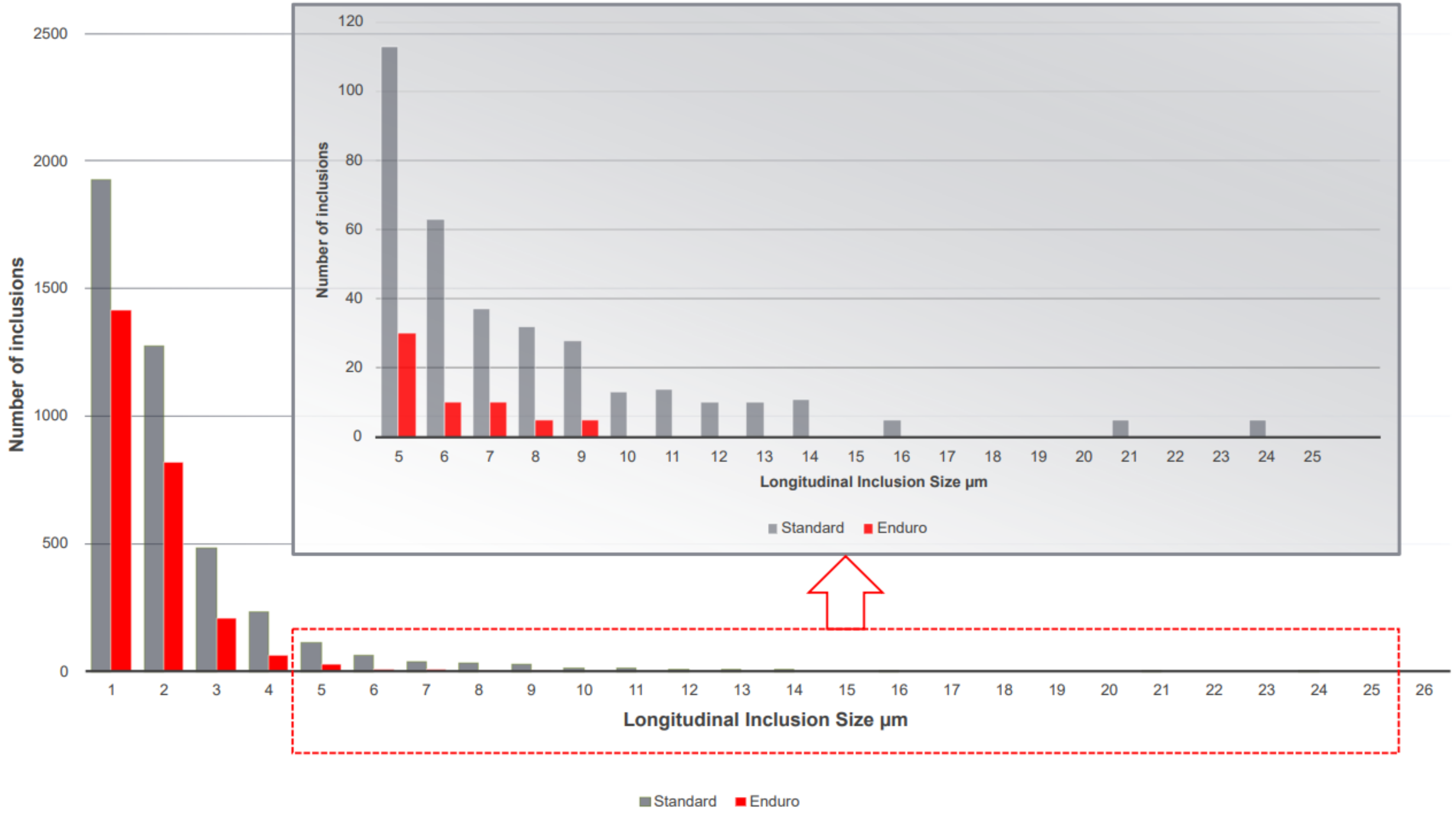
Wire z-specimen



[M. Launey et al., JMBBM, 34 (2014), p 181-186]

The Enduro Nitinol Alloy

- Engineered to reduce inclusion size and density through newly developed proprietary vacuum melting and optimized conversion processes
- ASTM F2063-18 compliant Nitinol ingot
- Available in all Nitinol product forms



The Enduro Nitinol Alloy

Robustness Testing / Specification Development

- Comprehensive robustness campaign executed to validate processes & develop inclusion specs.
  - 18 ingots produced in three separate melting campaigns of six ingots each
  - Total of 486 fields of view analyzed at 500x magnification from 6 mm coil and 25 mm bar
- Effectively eliminated non-metallic inclusions with length > 12 μm and greatly reduced inclusion density of particles over 1 μm
  - Density of >5 μm inclusions reduced 10x from standard VIM+VAR alloy!

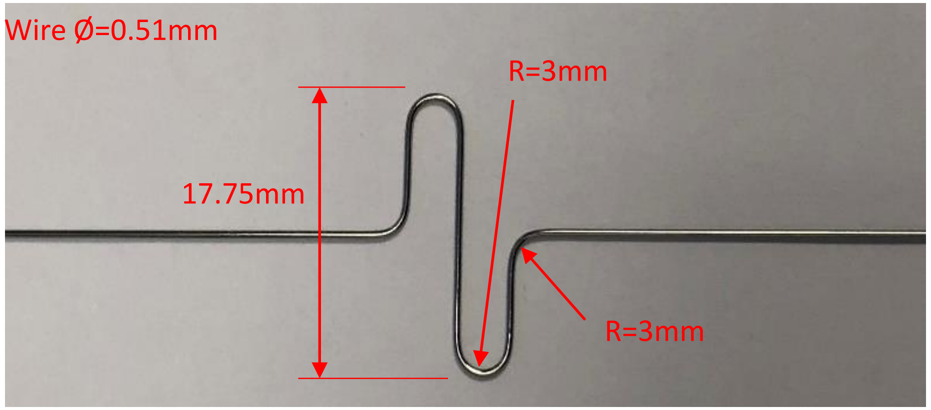
SAES Smart Materials (SSM) Alloy Inclusion Specifications

	Max Inclusion Size [μm]	Max Inclusion Area [%]
ASTM F2063-18 Requirement	39.0	2.8
SSM Standard	26.0	2.0
SSM Enduro	**12.0**	**0.5**

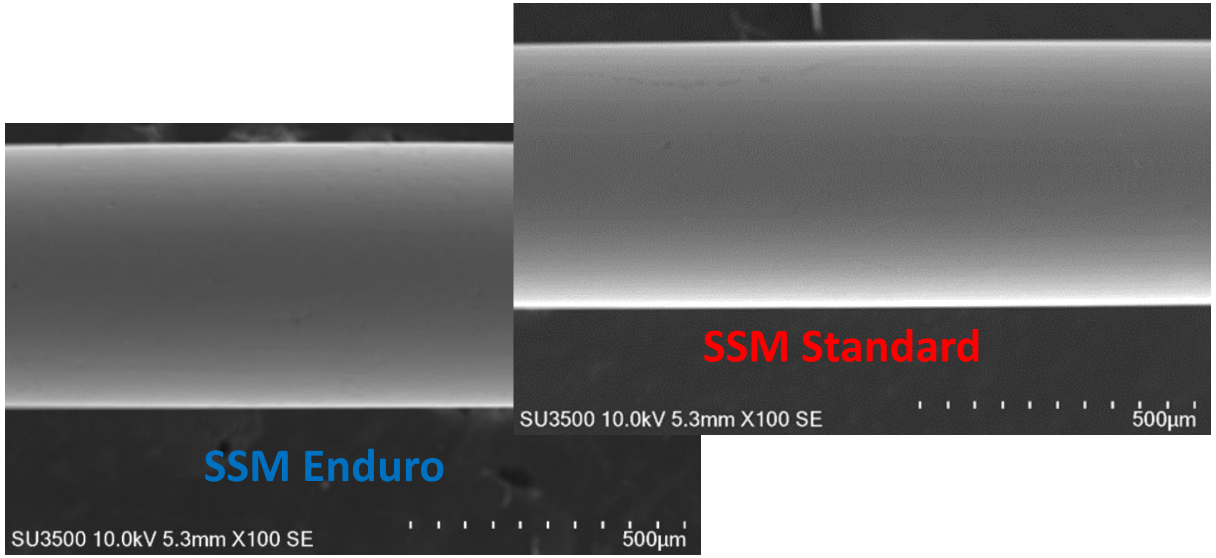
Experimental

Fatigue Sample Preparation (RBT & Z-Specimen)

- SSM standard and Enduro, A_s -15±10°C, ingots used in study
- 0.53mm (0.021”) wire drawn at Memry *using identical draw schedules*
- Shape set heat treatment → 2.5 min. @ 525°C in salt pot
- Surface Finish → Electropolished to 0.51mm (0.020”)



Z-specimen Geometry [K. Pike, et al. 2010]



Electropolished surface

Material Characterization

Inclusion & Composition Analysis

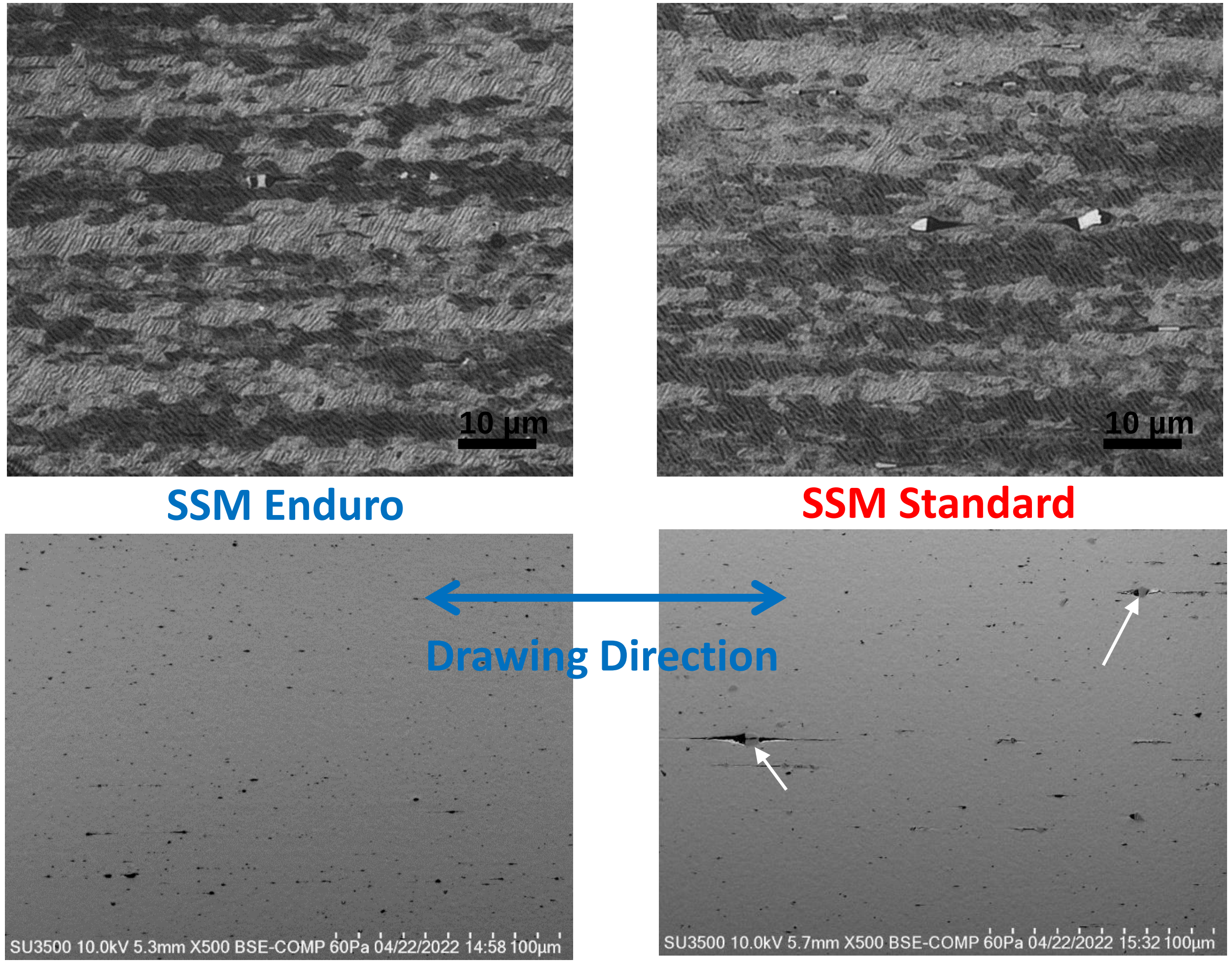
- Ingot inclusion analysis performed on 6 mm dia. coils with 27 fields of view at 500x magnification
- Enduro Oxygen and Carbon composition in line with average identified in robustness campaign (i.e. C → 258±18 ppm, O → 208±26ppm)

	Ingot Inclusion Analysis	
	MAX. Length (µm)	MAX. Area (%)
SSM Standard	16.0 – 17.53	0.56-0.94
SSM Enduro	8.05	0.27

Element	SSM Standard Value [wt.%]	SSM Enduro Value [wt.%]	ASTM F2063-18 Requirement [wt.%]
Ni	55.86 - 56.05	56.02	54.5 to 57.0
C	0.0313	0.0258	0.040 MAX.
Co	0.0001	0.0001	0.050 MAX.
Cu	0.0007	0.0001	0.010 MAX.
Cr	0.0031	0.0017	0.010 MAX.
H	< 0.0050	<0.0050	0.005 MAX.
Fe	0.013	0.009	0.050 MAX.
Nb	0.0001	0.0001	0.025 MAX.
N	0.0014	0.0012	0.005 MAX.
O	0.028	0.022	0.040 MAX.
Ti	Balance	Balance	Balance

Material Characterization

Wire Microstructure



Average Grain Size

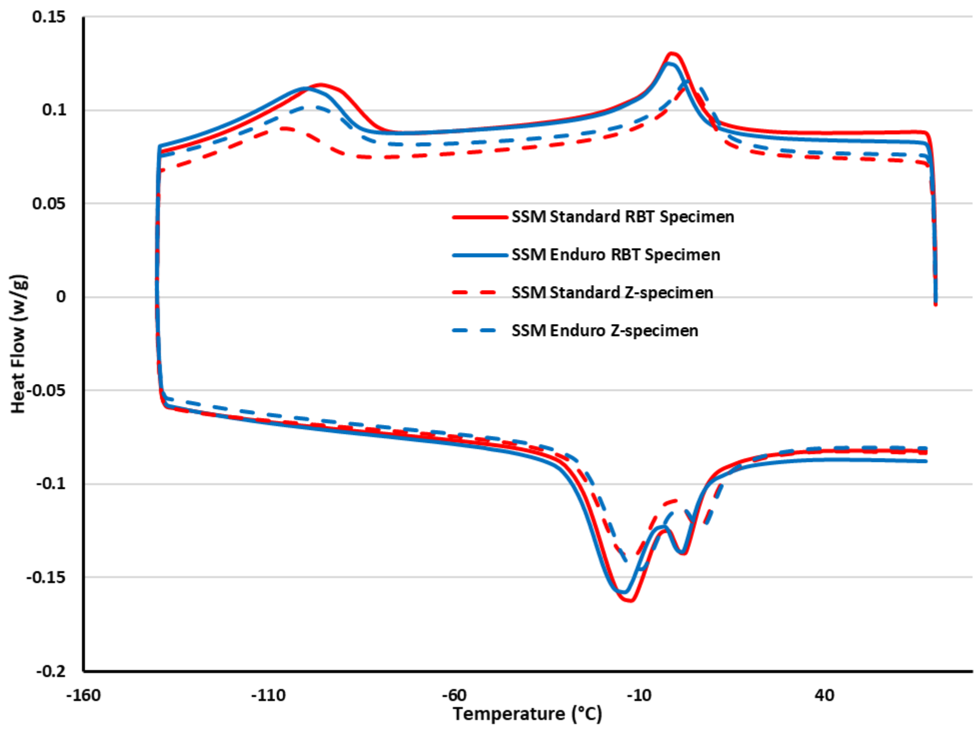
SSM Std.		SSM Enduro	
Longitudinal [µm]	Transverse [µm]	Longitudinal [µm]	Transverse [µm]
3.32 ± 0.70	1.46±0.26	3.52±0.71	1.55±0.42

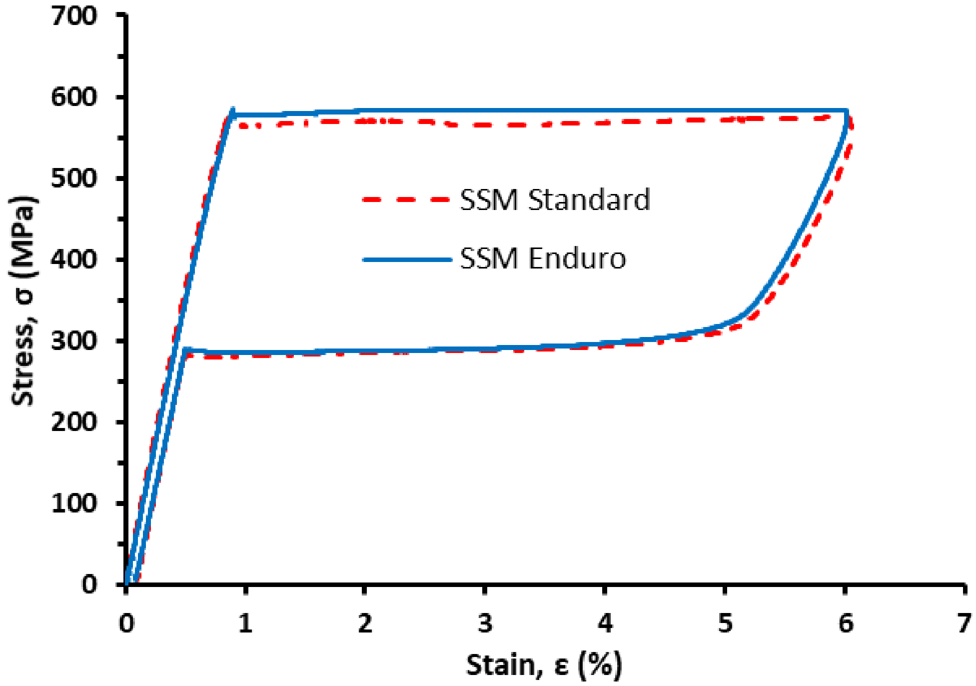
- Grain size verified to be similar between materials in both longitudinal and transverse directions
- Larger inclusions found in standard material lead to more voids and longer stringers in the drawn wire microstructure

Material Characterization

Thermomechanical Properties

- DSC performed per ASTM F2004-17 on non-annealed samples (i.e. final specimen conditions)
- Tensile Testing per ASTM F2516-18 performed at 37°C





Material Characterization

Material Property Summary

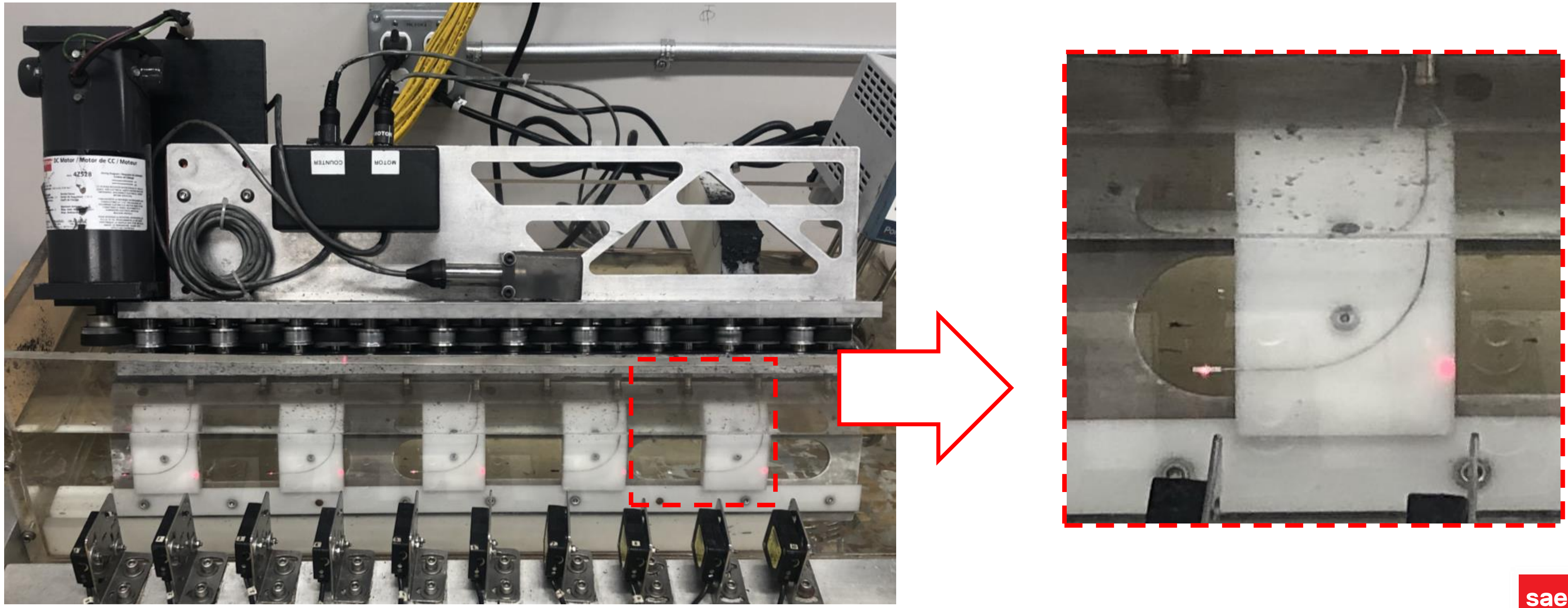
- Included Active Af results obtained from BFR for RBT specimen here (ASTM F2082-16)
- Extremely consistent thermomechanical properties realized when comparing samples produced from standard and Enduro ingots

	Specimen Type	DSC, Af (°C)	BFR, Active Af (°C)	UPS (MPa)	LPS (MPa)	UTS (MPa)
SSM Standard	RBT Specimen	8.81	3	565	288	1300
	Z-Specimen	15.3	-	-	-	-
SSM Enduro	RBT Specimen	10.01	4	583	288	1350
	Z-Specimen	14.97	-	-	-	-

Rotating Beam Testing (RBT)

In-house Testing per ASTM E2948-16a

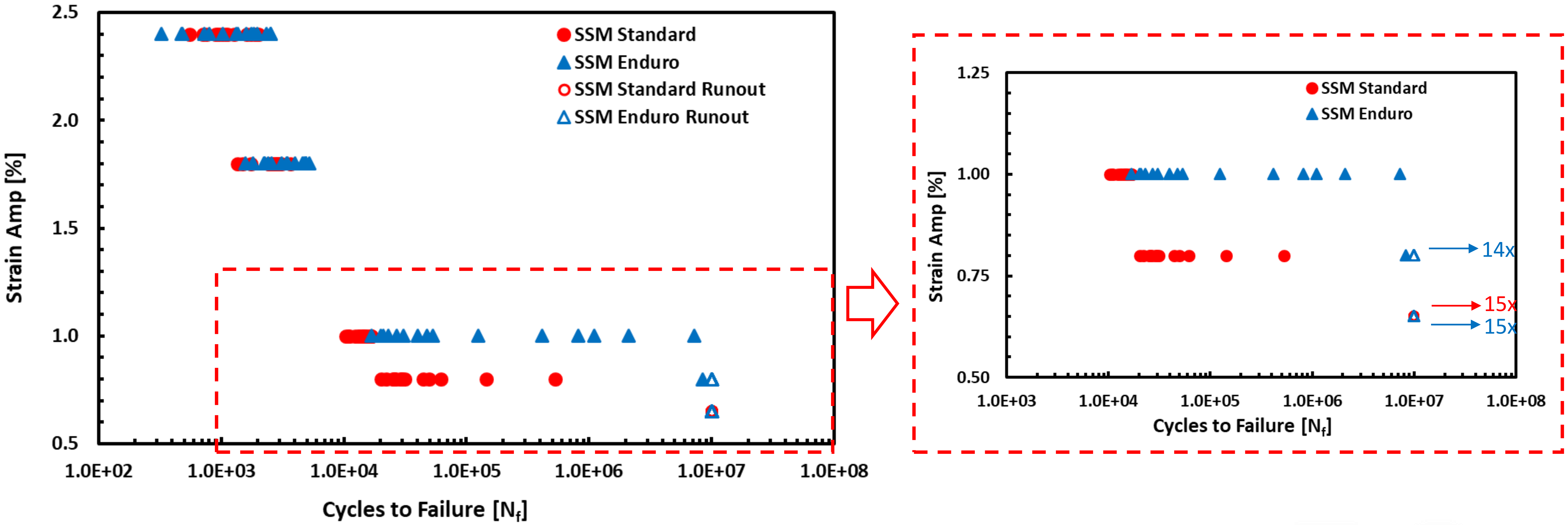
- **Test Conditions** → Mean strain = 0%, 1000 RPM, Strains = 2.4, 1.8, 1.0, 0.8 & 0.65 %, Temp. = 37°C
- Sample size, n=15
- Guided style rotating beam test setup with laser counter break detection



Rotating Beam Testing (RBT)

Results

- Enduro showing a significant improvement in high cycle fatigue



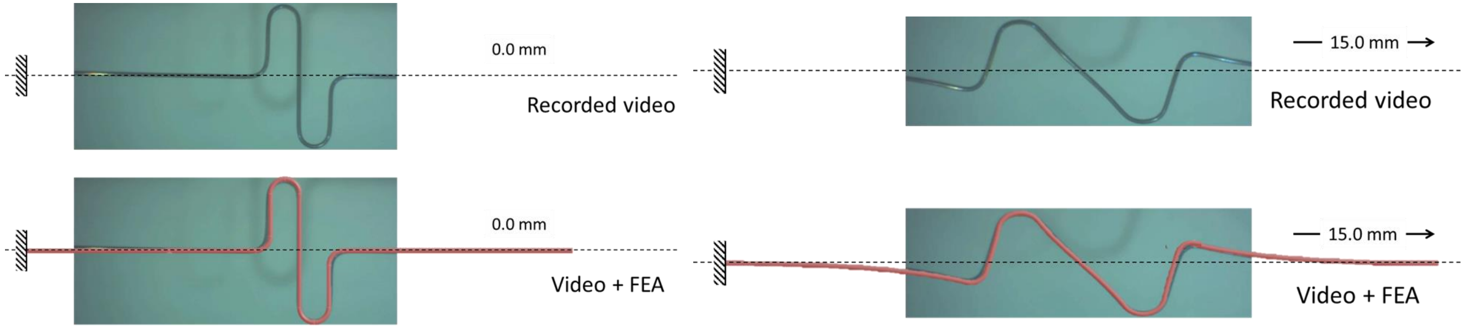
Z-Specimen Testing

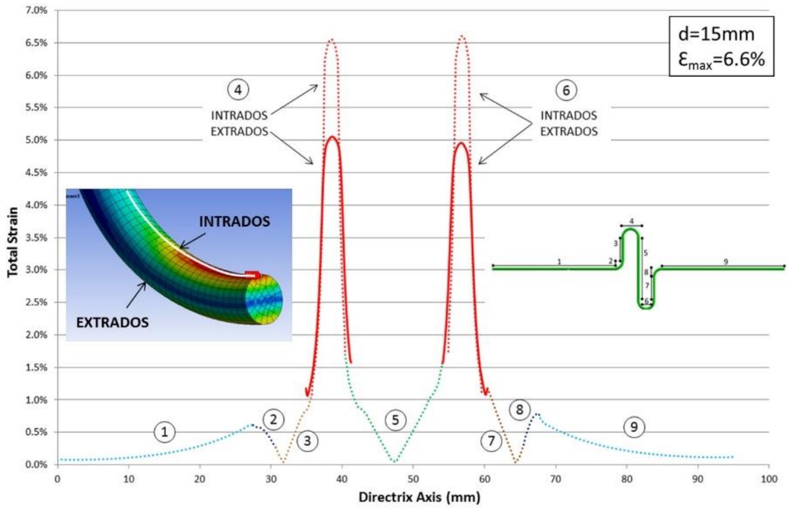
Z-specimen test designed to simulate z-stent application

- **Background** → Specimen developed by K. Pike et al. 2010 and a similar study performed by M. Launey et al. using the z-specimen in 2014

FEA Analysis

- Non-linear FEA analysis used to identify maximum strains
- Model created using material properties as inputs and validated using load displacement curves obtained from pull testing of z-specimen

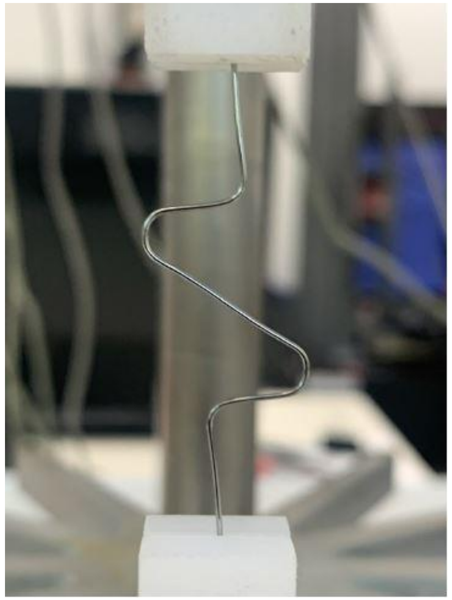


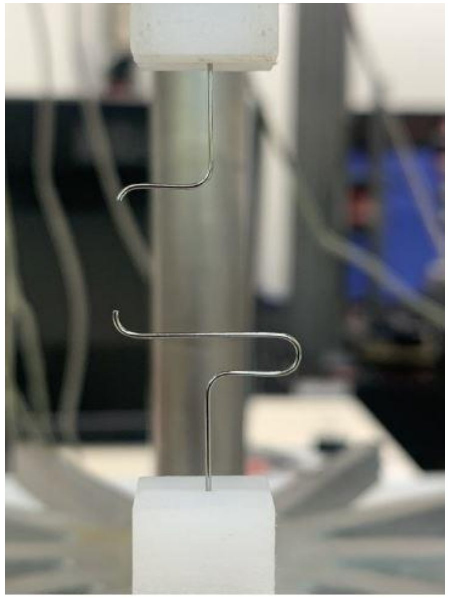


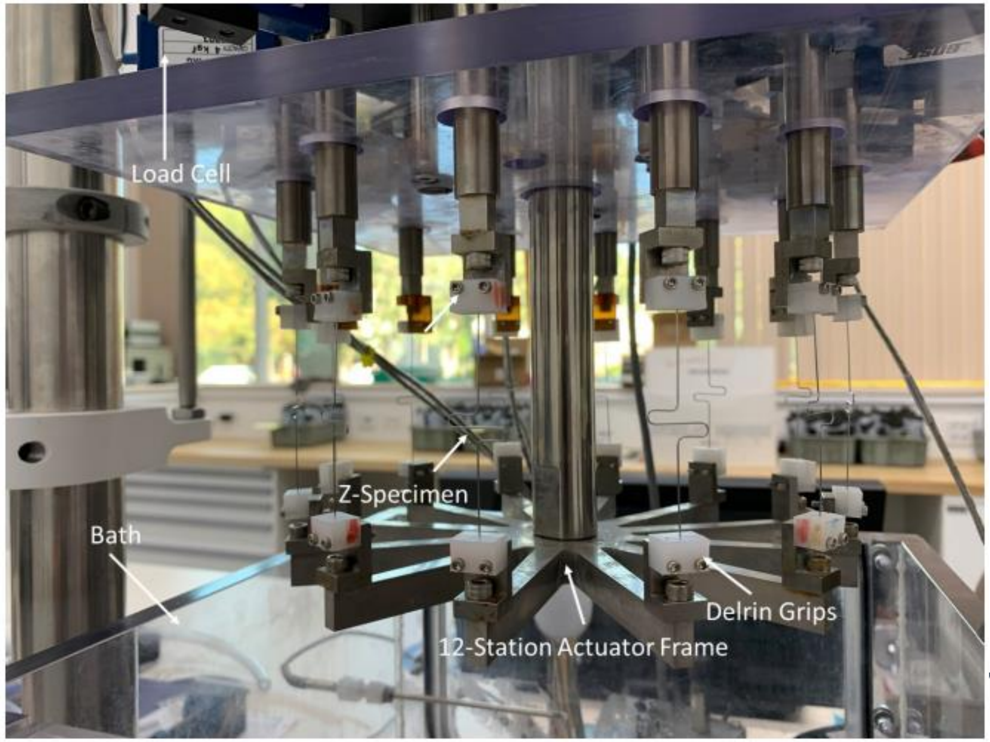
Z-Specimen Testing

Experimental - Outsourced Testing

- **Equipment** → 12-station BOSE ElectroForce Model 3330 multi-specimen fatigue tester
- **Bath conditions** → 37°C, PBS solution
- **Frequency** → 20 – 30 Hz for high to low strain amplitude conditions respectively
- **Strains** → Mean = 3.5%, Amplitudes = 2.5, 2.0, 1.5, 1.3, 1.0, and 0.5 %
- n=12 samples



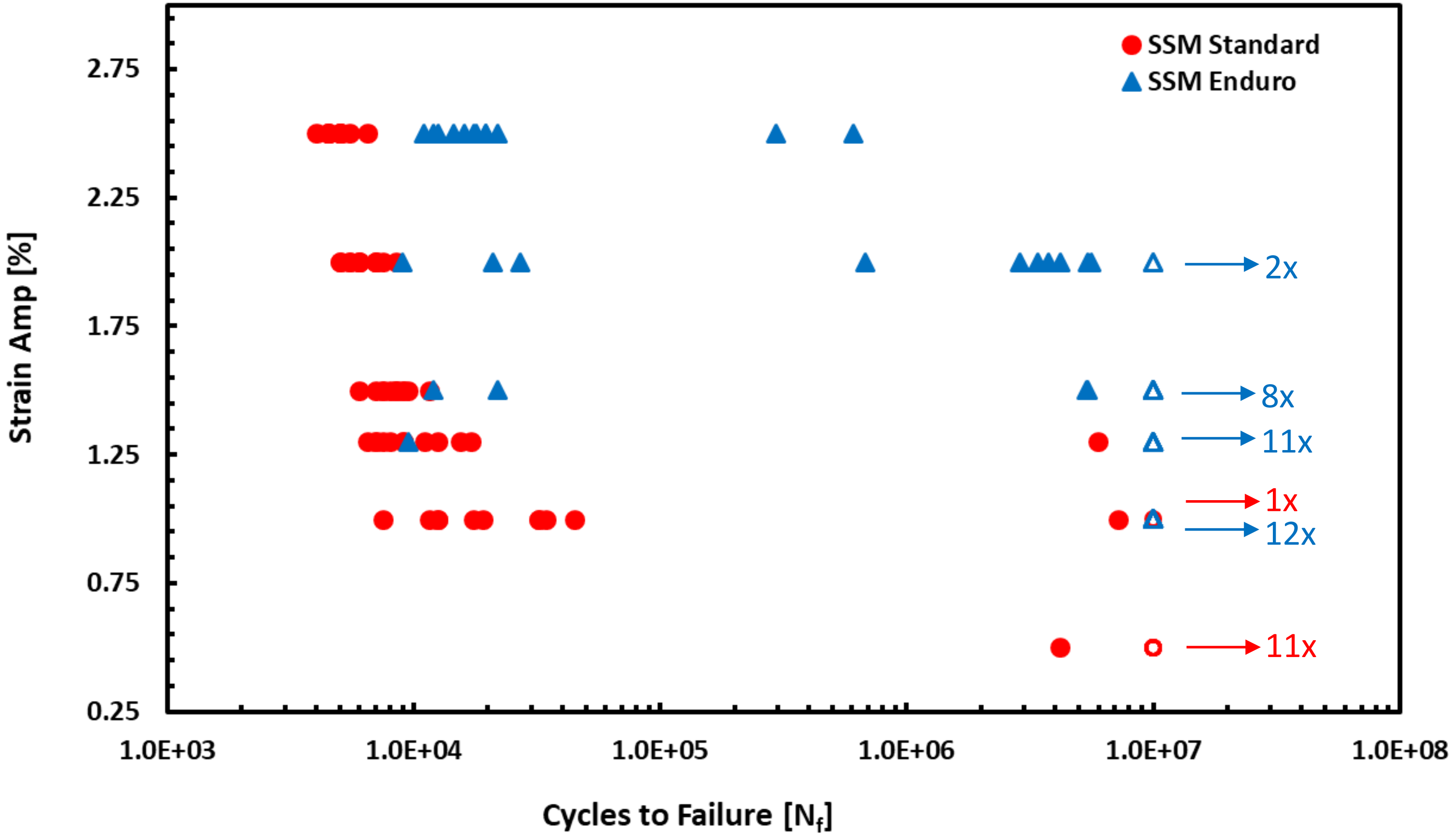


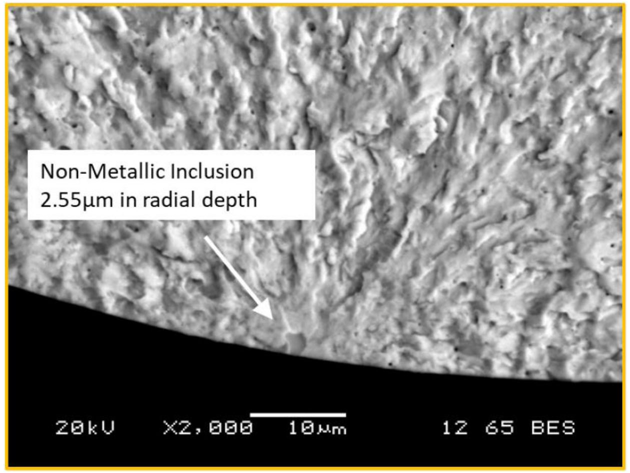


Z-Specimen Testing

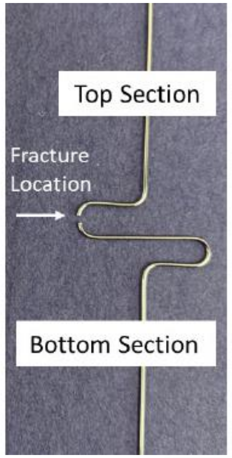
Results

- Enduro out performed the standard material at all strain conditions in this 3.5% mean strain fatigue test





- All samples failed at apex. as expected

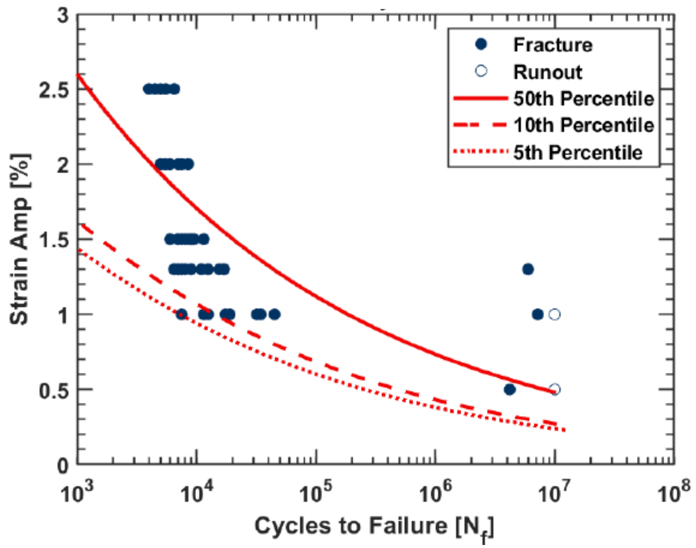


Z-Specimen Testing

Fatigue Limit at 10^7 Cycles

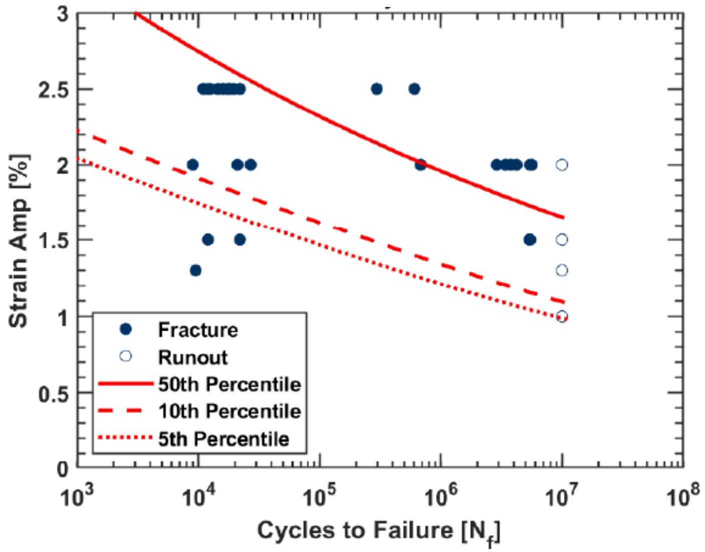
- **4.2x** improvement in fatigue limit at 10^7 cycles calculated using Lognormal regression fit with 95% confidence

SSM Standard



Percentile	10^7 Cycle Fatigue Limit
50th	0.48%
10th, 90% Confidence	0.27%
5th, 95% Confidence	**0.23%**

SSM Enduro



Percentile	10^7 Cycle Fatigue Limit
50th	1.65%
10th, 90% Confidence	1.09%
5th, 95% Confidence	**0.98%**

Summary

- Consistent Nitinol thermomechanical properties are achieved using both SSM standard and Enduro wrought materials without any changes required to downstream processes

- Greatly improved fatigue performance was demonstrated in both RBT and Z-specimen fatigue testing when using the Enduro Nitinol material due to smaller non-metallic inclusion size and lower inclusion density

SMST2022
Shape Memory and Superelastic Technologies Conference and Exposition

The Westin Carlsbad
San Diego, CA
May 16– 20, 2022

The Assessment of Physical and Mechanical Property Variability in a New Generation of Ultra-low Inclusion NiTi Alloy

Dr. Weimin Yin, Frank Sczerzenie, Rich LaFond

SAES Smart Materials, Inc

saes group

making innovation happen, together

Background and Motivation

Medical device designers continually innovate, often challenging Nitinol durability boundaries

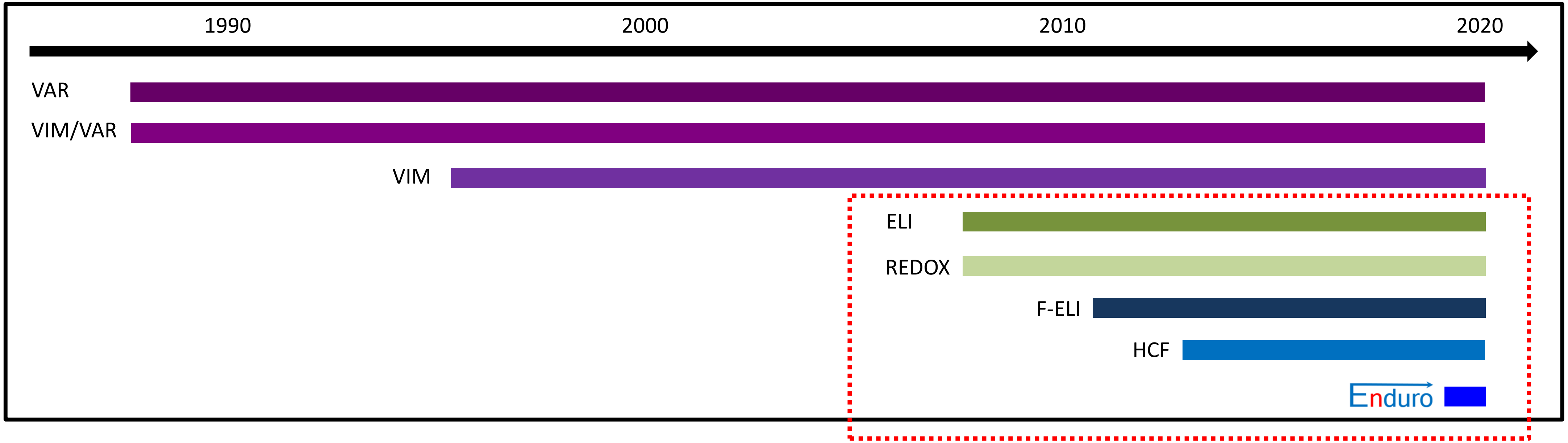
- Smaller features
- More complex applications
- Higher cycles to failure

Device durability is primarily affected by:

- Application
- Design
- Component processing and surface finish
- Raw material micro-cleanliness

Background and Motivation

Major Commercially Available Nitinol Alloys



Nitinol Suppliers have responded in recent years by improving their Raw Material offer

Background and Motivation

This newest, cleanest offering from SAES Smart Materials, Inc. was engineered for ultra-demanding applications by minimizing the size of non-metallic inclusions

Enduro Highlights

- Development started 2017 and was commercially released 2021
- Proprietary commercial scale melting process
- Optimized conversion process
- Available in all Nitinol product forms, ASTM F2063 compliant

Process robustness and consistency was deemed critical and was extensively challenged prior to market release in 2021

This important work will be summarized in the presentation

Experimental Procedures and Planned Studies

Enduro Process Robustness Study

- 18 commercial scale heats were melted in 3 discrete campaigns of 6 heats each
- Each campaign was separated by at least 4 weeks to capture variability in raw materials, melting and downstream processing
- Evaluation was performed on hot rolled products: 6 mm diameter coils and 25 mm diameter bars

Characterization per ASTM F2063-18

- Chemistry
- Mechanical properties
- Microstructure

Micro-cleanliness Characterization and Analysis

Sampling Plan for Inclusion Characterization

- 3 locations along ingot length, each checked at 3 radius positions
- 3 images taken at all 9 sites, totaling 27 micrographs per ingot (~ 1 mm^2 area analyzed)
- Two cross-sections at each site (longitudinal per ASTM F2063 and transverse)

Consistent protocol as used for standard production

- Olympus AX70 optical microscope with a Teledyne Retiga 6 camera
- Image processing through Image Pro 10 software

Micro-cleanliness Analysis

- Inclusion maxima, Inclusion density, Gumbel distribution

Consistency of Main Gas Impurities

Carbon
- 258 ppm average
- 18 ppm standard deviation

Oxygen
- 208 ppm average
- 26 ppm standard deviation

Trace impurities not reported in table but consistent with standard nitinol

Campaign	Ingot	C, ppm	O, ppm	N, ppm
E1	E1-1	280	210	7
	E1-2	237	210	<5
	E1-3	226	250	<5
	E1-4	244	240	<5
	E1-5	229	230	<5
	E1-6	247	240	<5
E2	E2-1	299	210	23
	E2-2	255	230	17
	E2-3	271	220	8
	E2-4	258	220	12
	E2-5	261	220	15
	E2-6	277	200	10
E3	E3-1	255	160	<5
	E3-2	259	170	<5
	E3-3	244	170	<5
	E3-4	263	190	5
	E3-5	260	200	<5
	E3-6	275	180	<5

Transformation Temperature Consistency (As)

DSC per ASTM F2004

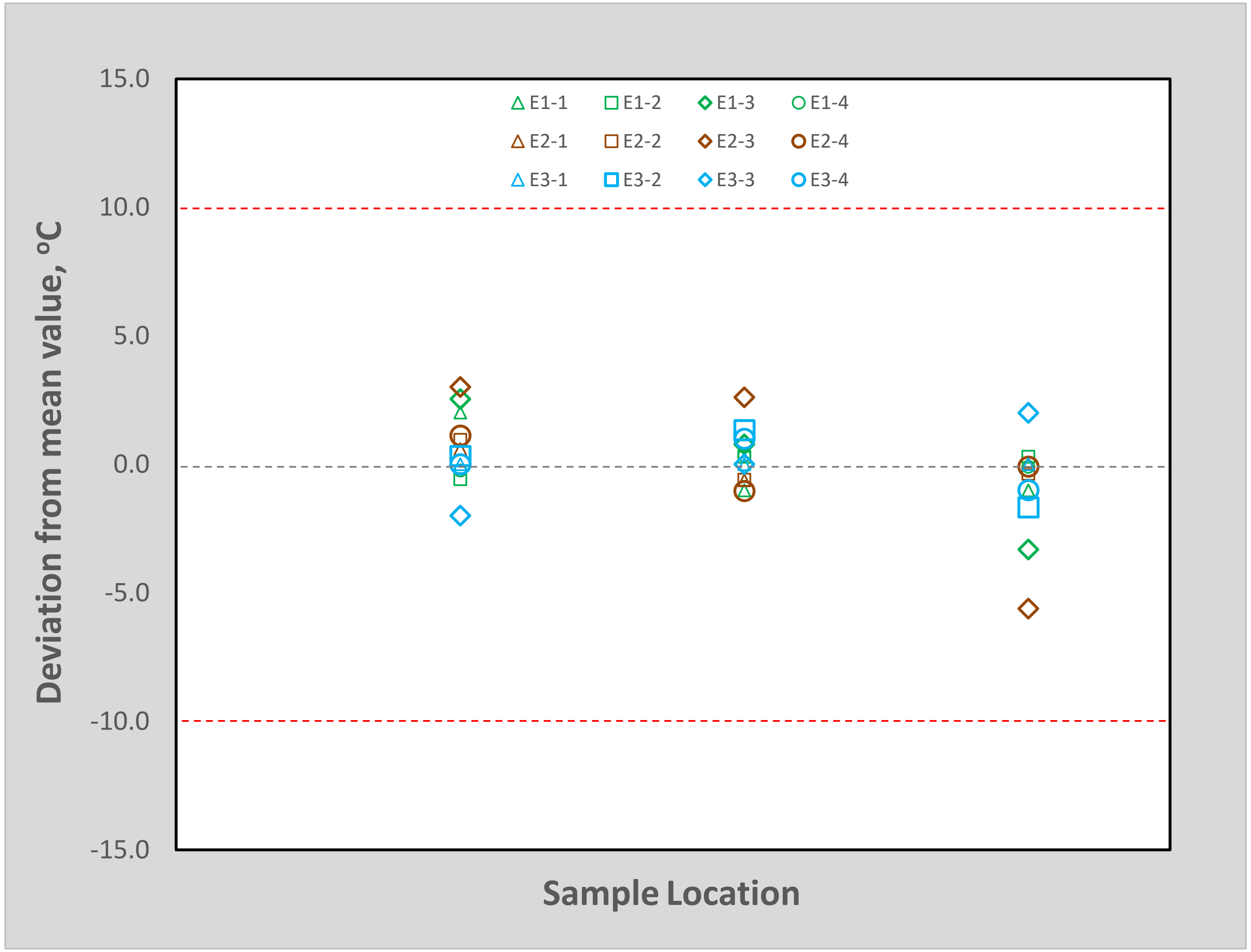
- 6 mm diameter coils
- Annealed at 850°C for 30 min.

Examine each ingot at 3 locations

- Variation ~ 5°C As in each ingot

ASTM F2063-18

- Stated tolerance of +/- 10°C



Properties of Mill Products

Tensile Tests per ASTM E8/E8M

- Specimens from bars and coils
- Annealed at 850°C for 30 min

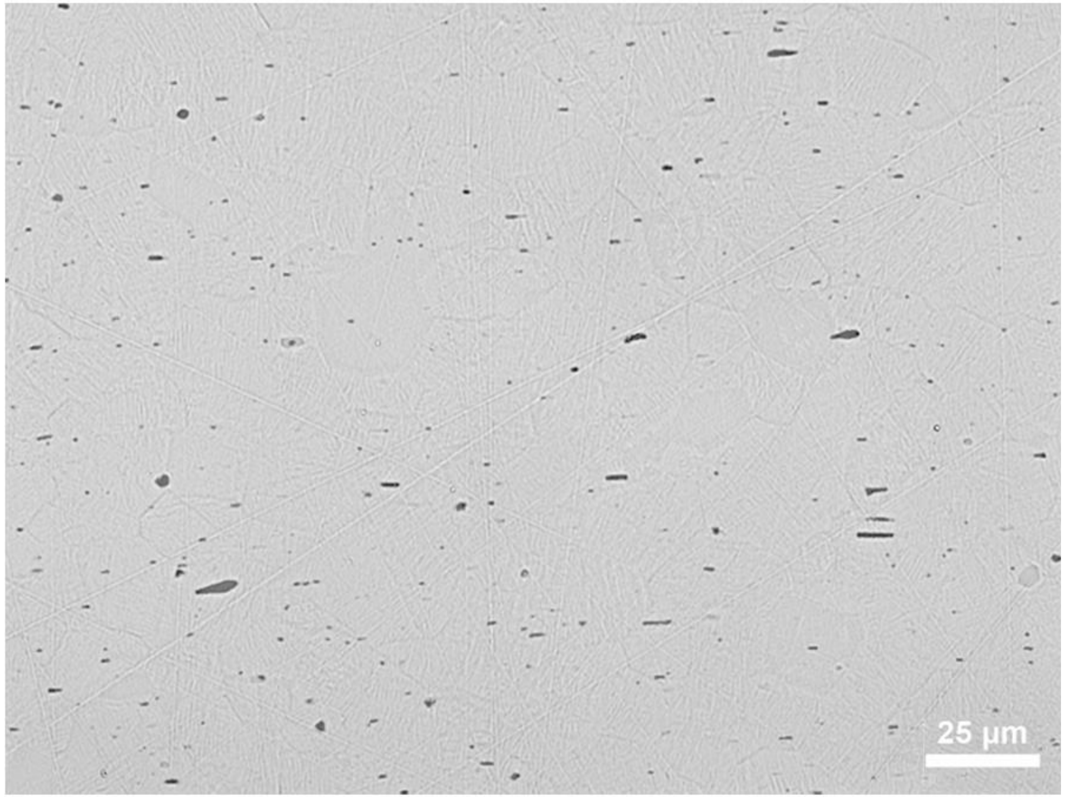
Grain size per ASTM E112

- All coils: ASTM G = 8
- All bars: ASTM G = 6

Campaign	Ingot	Product Type	Product Size, mm	Grain Size, ASTM G	UTS, MPa	Elongation, %
E1	E1-1	Coil	6	8	641	15
	E1-2				752	31
	E1-3				724	24
	E1-4				738	30
	E1-5	Bar	25	6	666	16
	E1-6				678	23
E2	E2-1	Coil	6	8	634	19
	E2-2				655	22
	E2-3				648	18
	E2-4				641	21
	E2-5	Bar	25	6	646	17
	E2-6				667	17
E3	E3-1	Coil	6	8	621	21
	E3-2				607	20
	E3-3				683	23
	E3-4				648	23
	E3-5	Bar	25	6	712	19
	E3-6				689	18
ASTM F2063-18			5.50-94.0	≥ 4	≥ 551	≥ 15

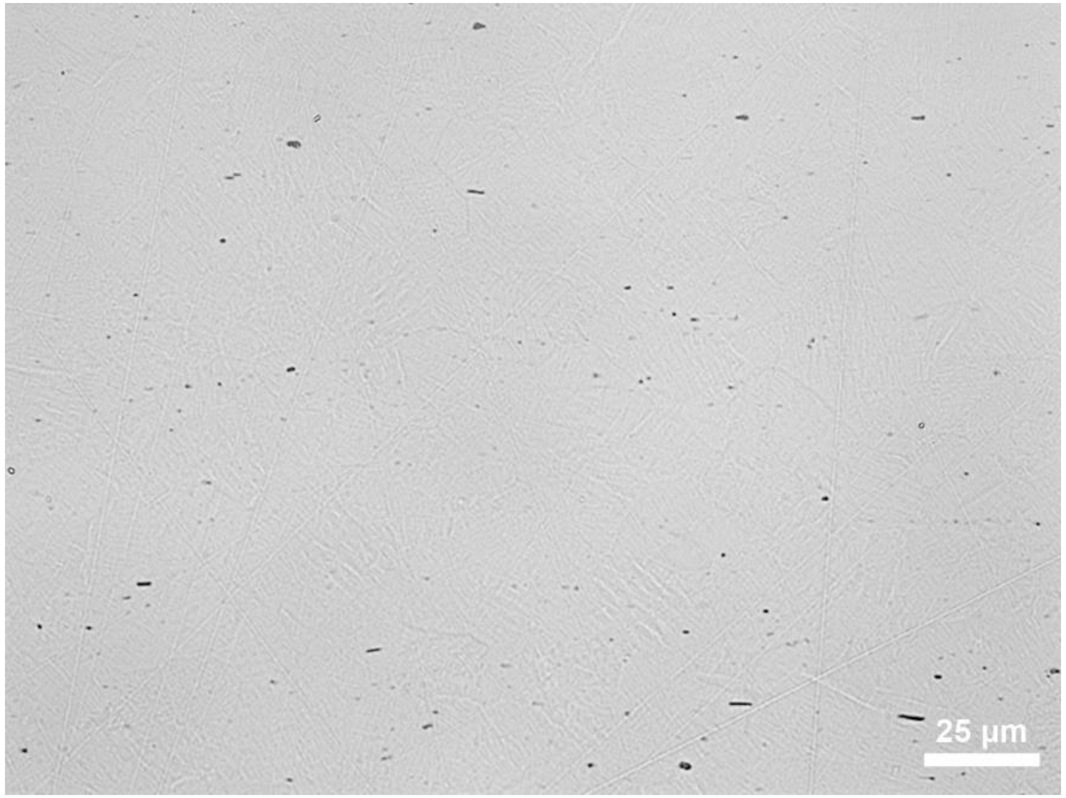
Microcleanliness – Longitudinal Section

Representative microstructure of Enduro and standard materials.



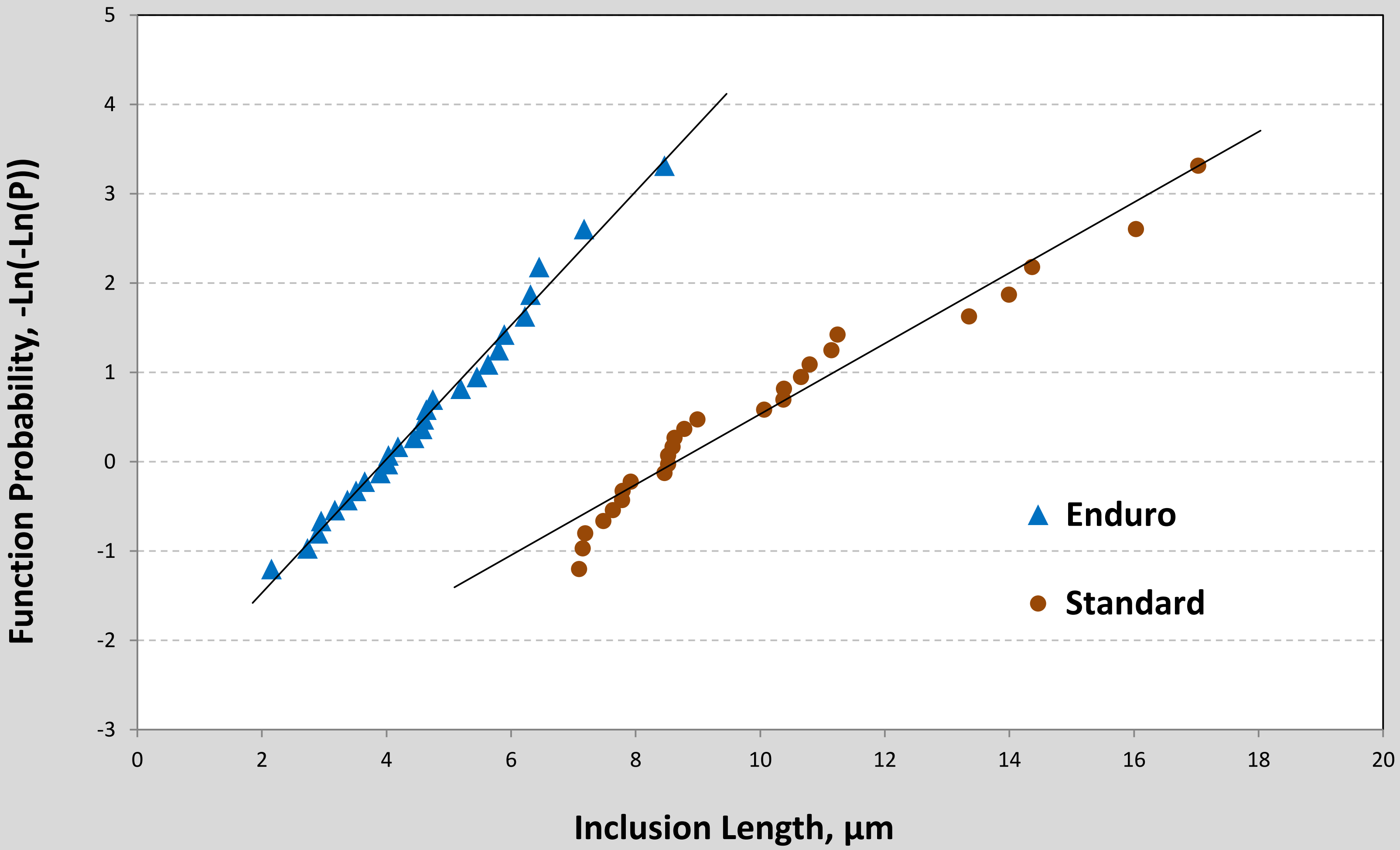
Standard

Rolling Direction



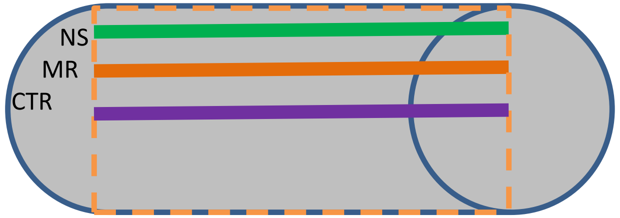
Enduro

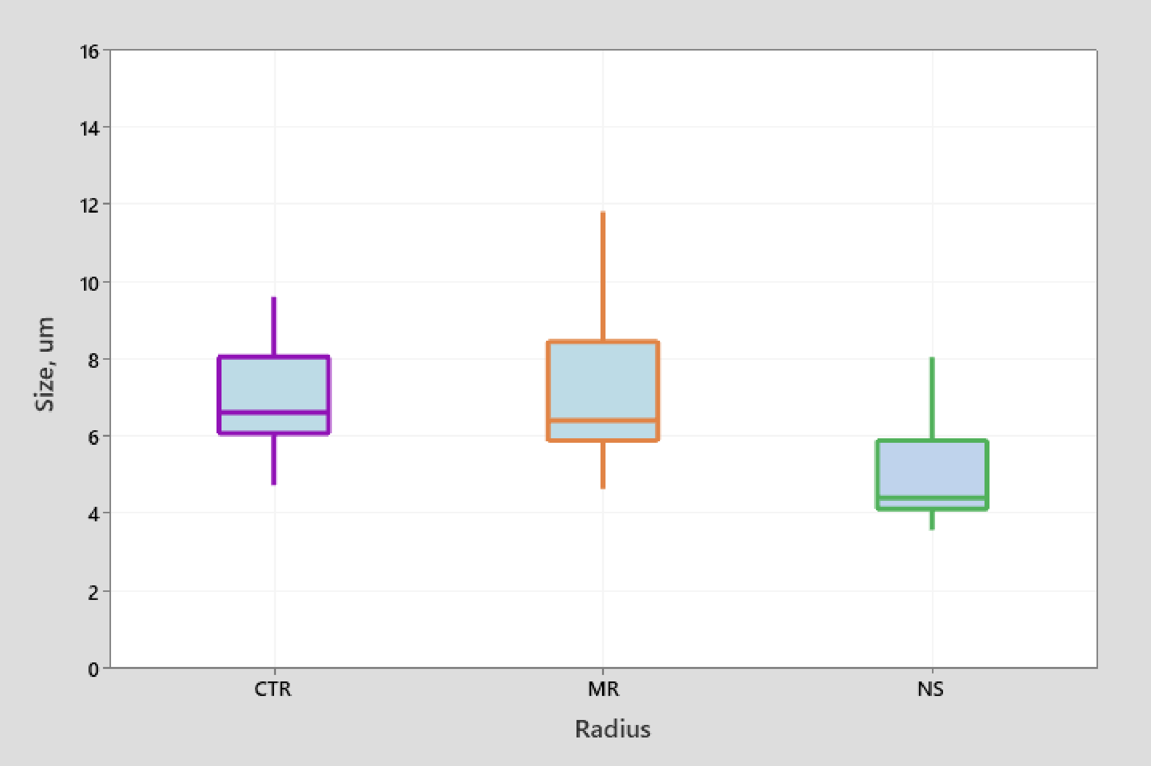
Longitudinal Inclusions – Gumbel Distribution

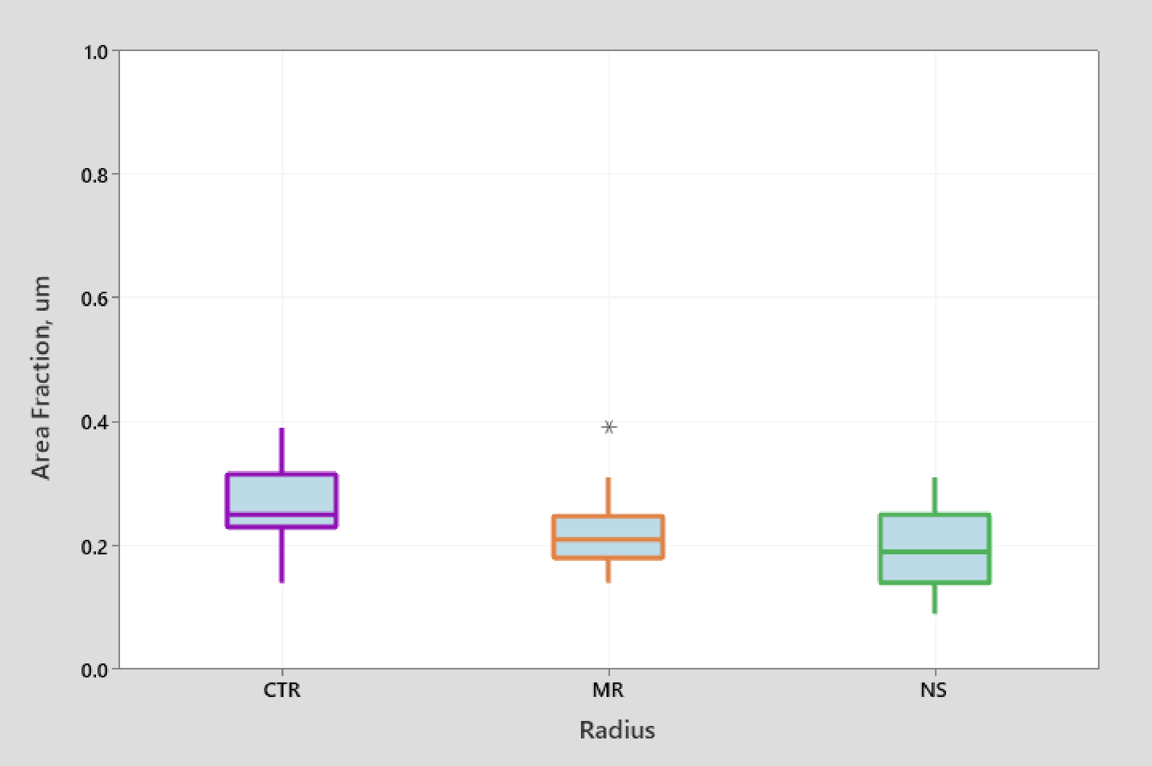


Radius Distribution of Inclusion Maxima

Longitudinal Inclusions in Enduro material
at center (CTR), mid-radius (MR) and near surface (NS)







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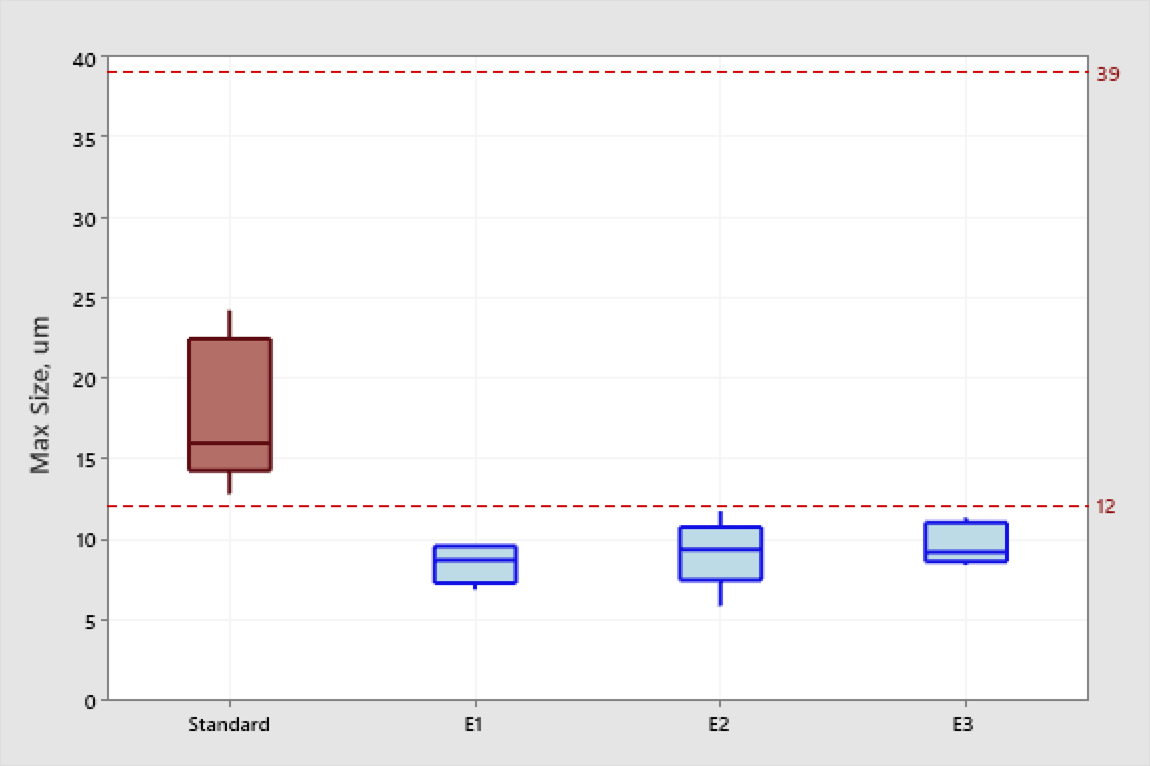
Longitudinal Inclusions Characteristics

Campaign	Ingot	Product		Longitudinal Inclusions		Inclusions Density, count/mm^2			
		Type	Size, mm	Max. Size, µm	Max. Area, %	> 1 µm	> 2 µm	> 5 µm	> 10 µm
E1	E1-1	Coil	6	8.3	0.36	1424	403	15	0
	E1-2			9.6	0.28				
	E1-3			9.7	0.37				
	E1-4			9.2	0.25				
	E1-5	Bar	25	6.9	0.33				
	E1-6			7.5	0.27				
E2	E2-1	Coil	6	9.7	0.46	1725	517	20	1.0
	E2-2			11.8	0.39				
	E2-3			10.5	0.44				
	E2-4			8.1	0.27				
	E2-5	Bar	25	9.1	0.42				
	E2-6			5.9	0.37				
E3	E3-1	Coil	6	8.9	0.22	1047	310	18	0.6
	E3-2			9.6	0.25				
	E3-3			8.5	0.23				
	E3-4			11.4	0.22				
	E3-5	Bar	25	11.0	0.30				
	E3-6			8.7	0.37				

Longitudinal Inclusions Maxima

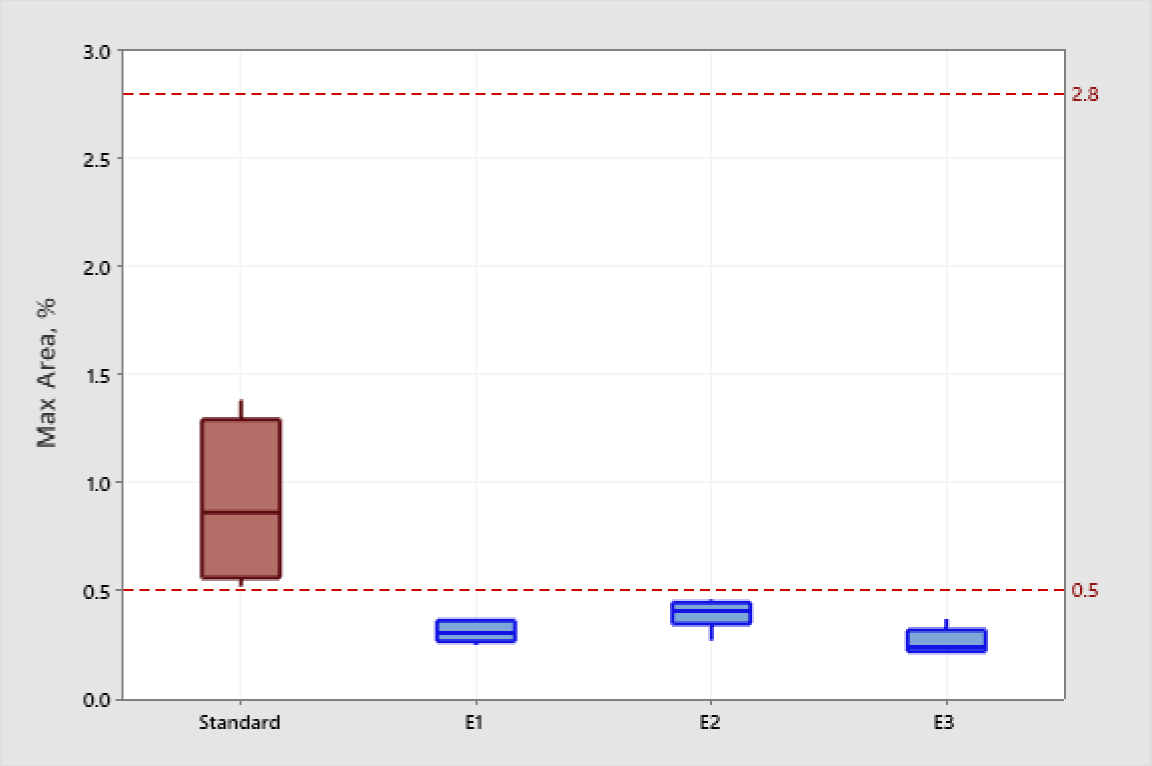
Inclusions Size

Eliminated large inclusion particles > 12 µm in Enduro



Inclusions Area Fraction

Reduced inclusion area fraction below 0.5 % in Enduro



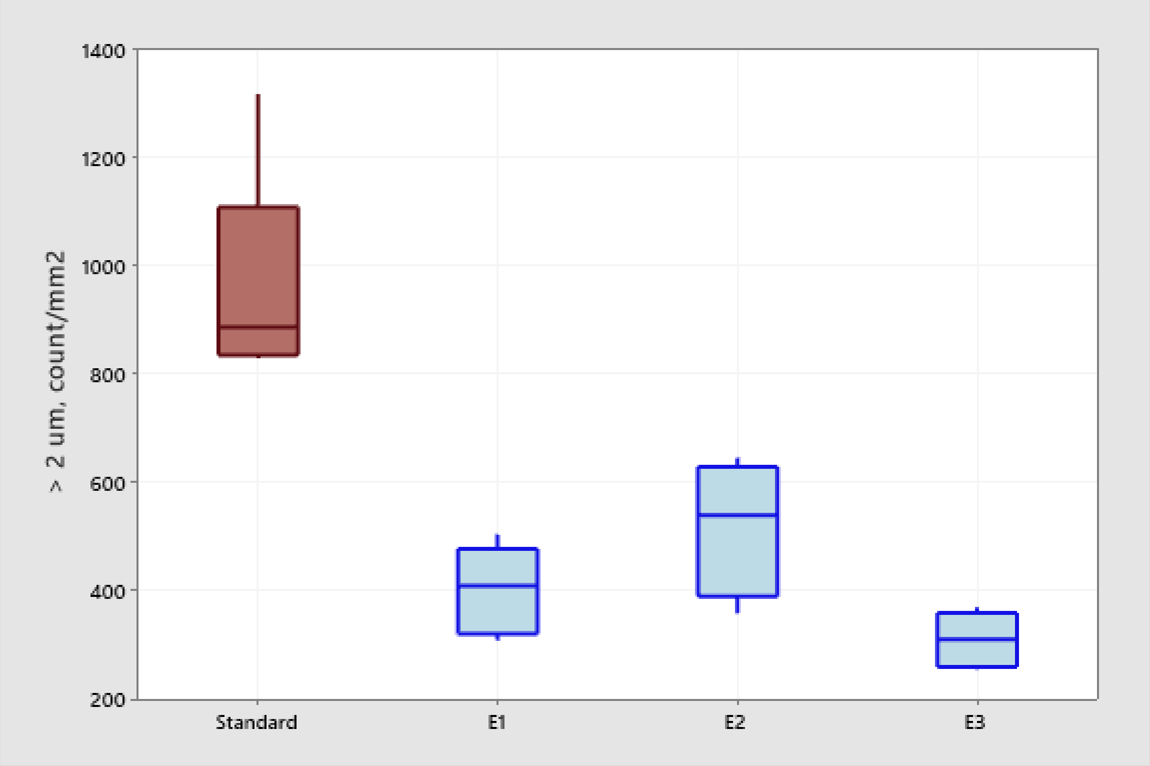
Longitudinal Inclusions Density

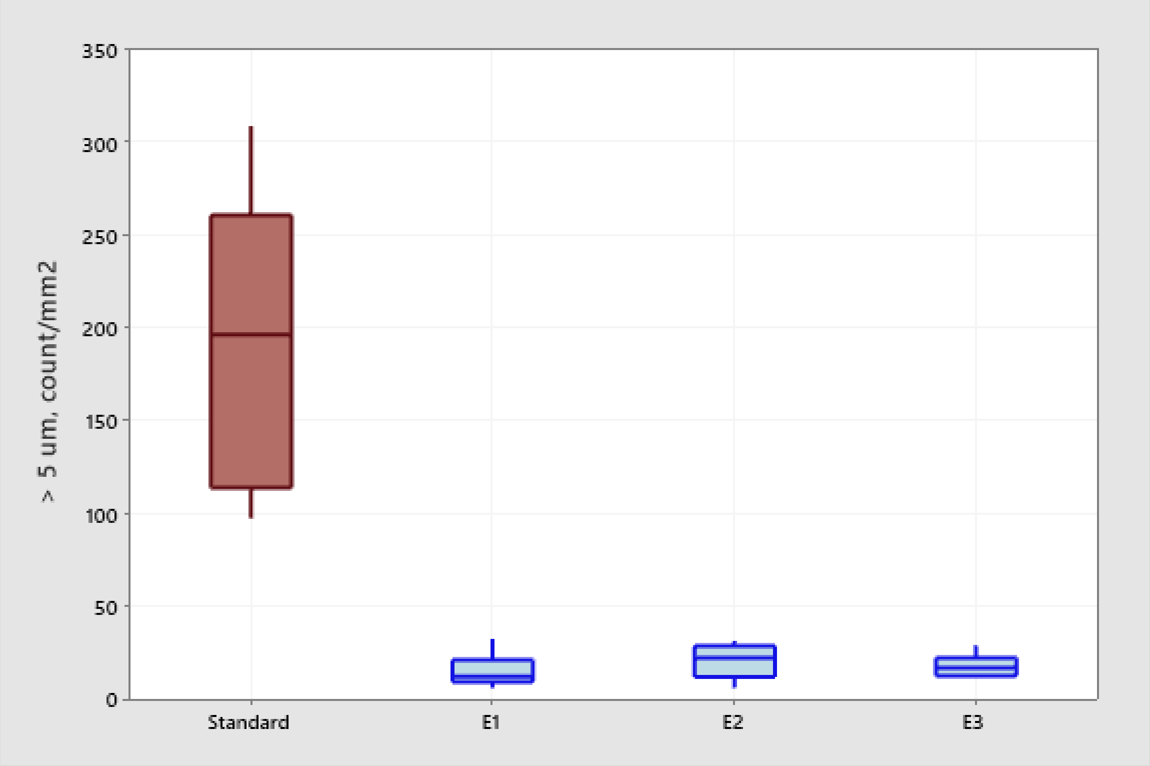
Inclusions > 2 µm

Inclusion density in Enduro has been reduced by ~ 2X

Inclusions > 5 µm

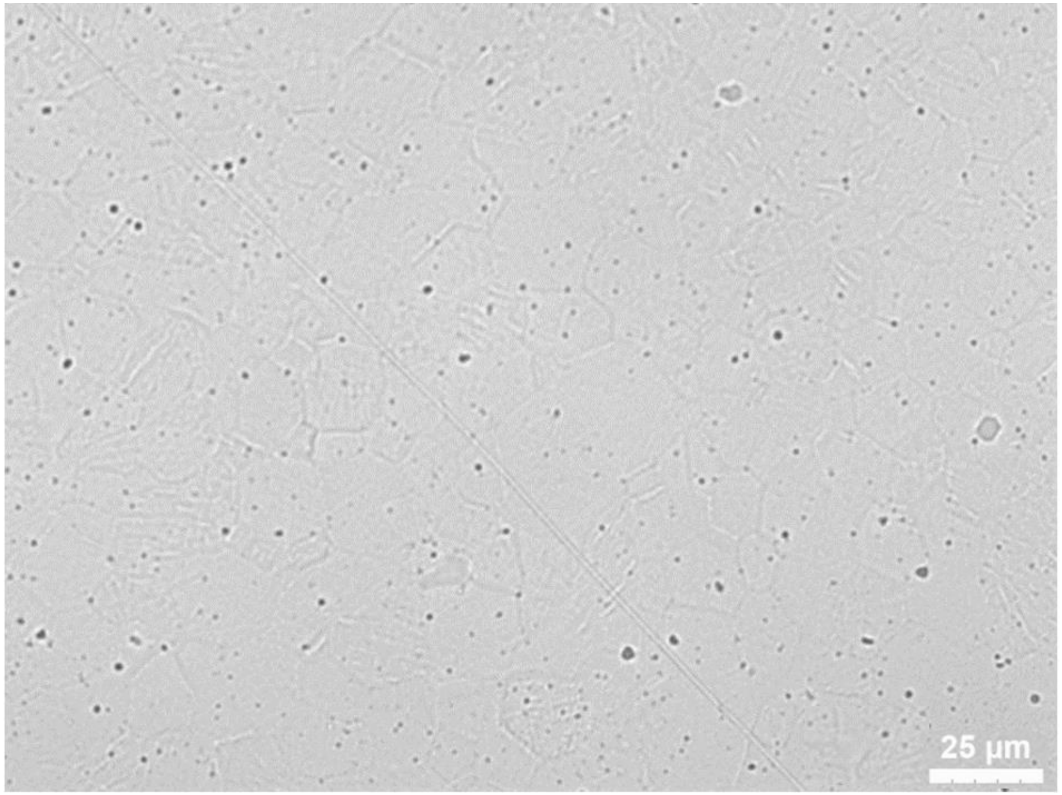
Inclusion density in Enduro has been reduced by ~ 10X

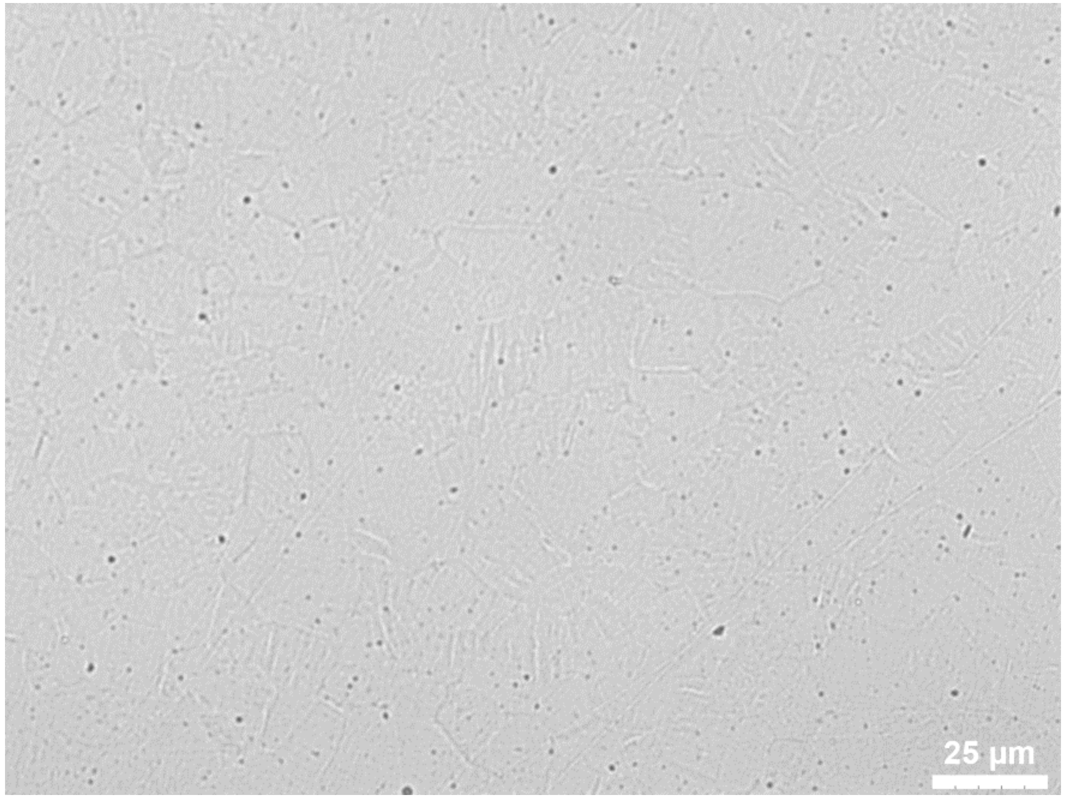




Microcleanliness – Transverse Section

Representative microstructure of Enduro and standard materials.

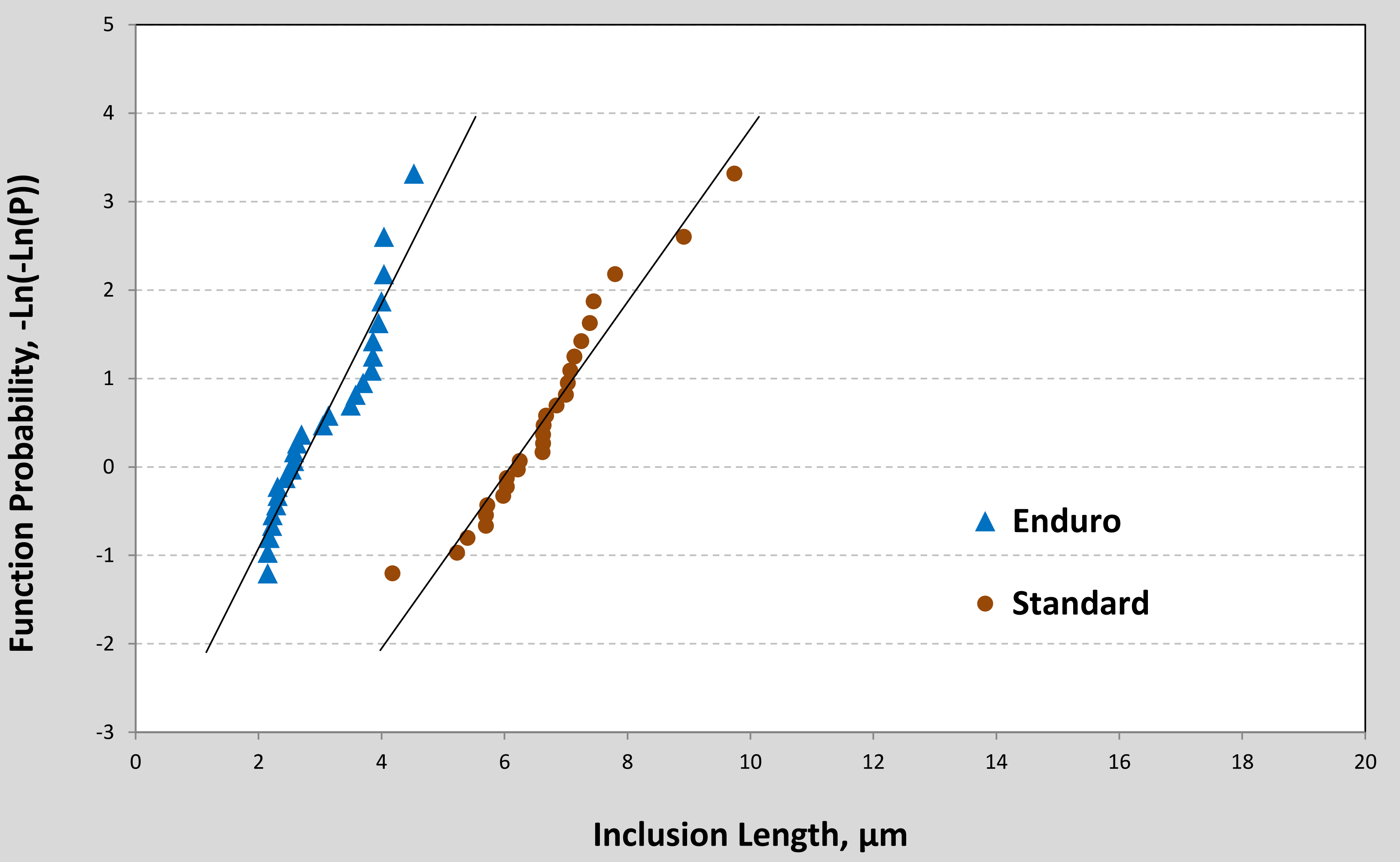




Standard

Enduro

Transverse Inclusions – Gumbel Distribution



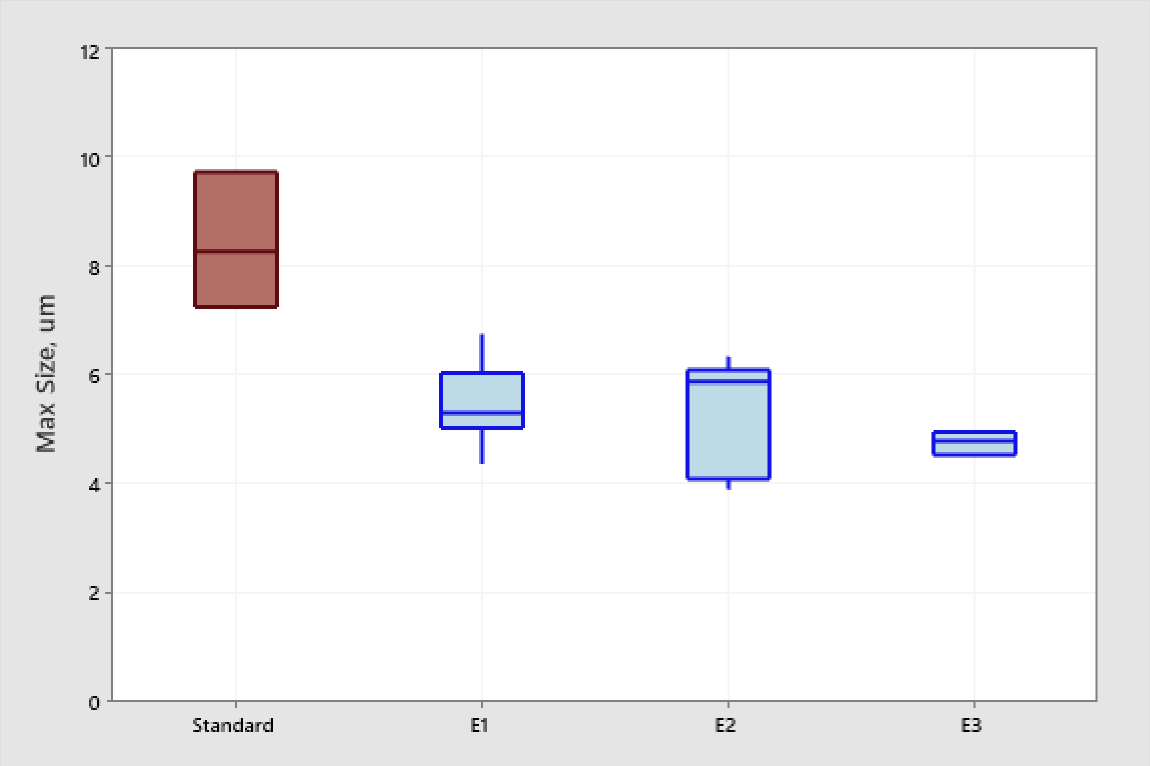
Transverse Inclusions Characteristics

Campaign	Ingot	Product		Transverse Inclusions		Inclusions Density, count/mm^2			
		Type	Size, mm	Max. Size, µm	Max. Area, %	> 1 µm	> 2 µm	> 5 µm	> 10 µm
E1	E1-1	Coil	6	5.3	0.34	1112	139	2.9	0
	E1-2			4.4	0.31				
	E1-3			6.8	0.36				
	E1-4			5.3	0.30				
	E1-5	Bar	25	5.3	0.39				
	E1-6			5.8	0.29				
E2	E2-1	Coil	6	4.1	0.35	1147	134	1.1	0
	E2-2			5.9	0.37				
	E2-3			5.1	0.40				
	E2-4			6.1	0.34				
	E2-5	Bar	25	6.3	0.43				
	E2-6			6.0	0.37				
E3	E3-1	Coil	6	3.9	0.27	1167	132	0.2	0
	E3-2			5.0	0.33				
	E3-3			4.5	0.32				
	E3-4			4.6	0.32				
	E3-5	Bar	25	4.8	0.38				
	E3-6			4.9	0.35				

Transverse Inclusions Maxima

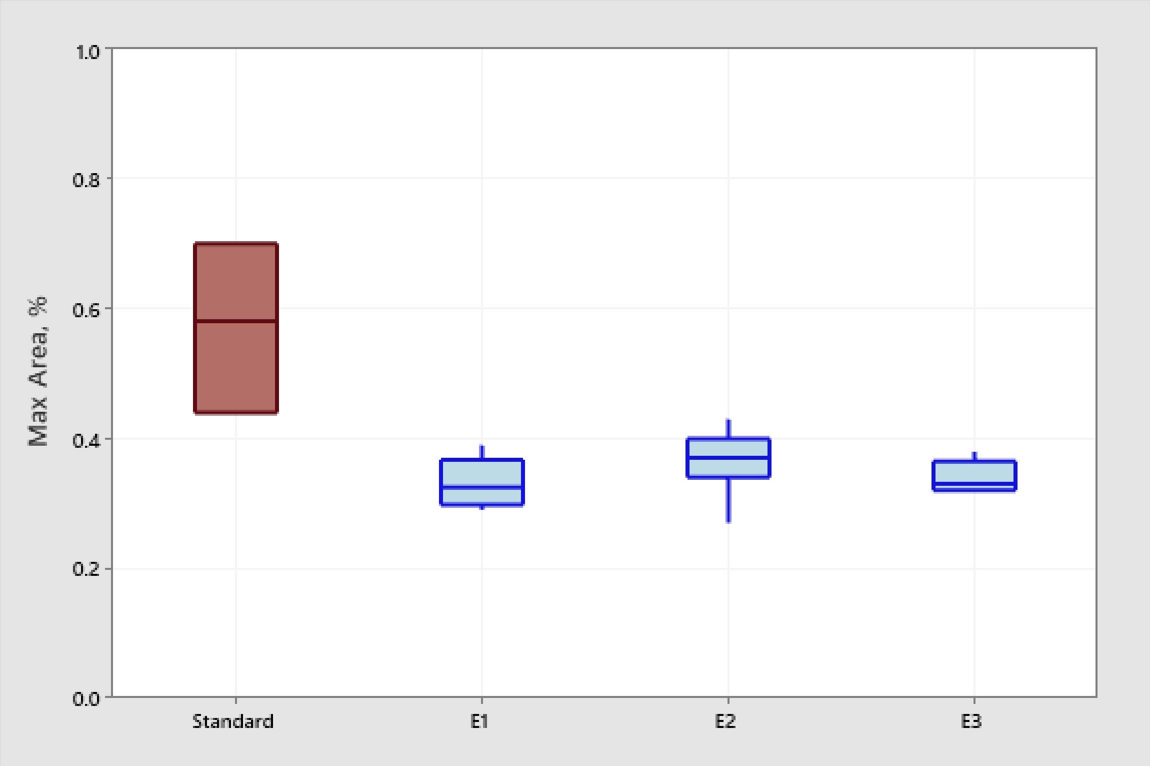
Inclusions Size

Reduced inclusion size about 100% in Enduro



Inclusions Area Fraction

Lowered inclusion area fraction about 100% in Enduro



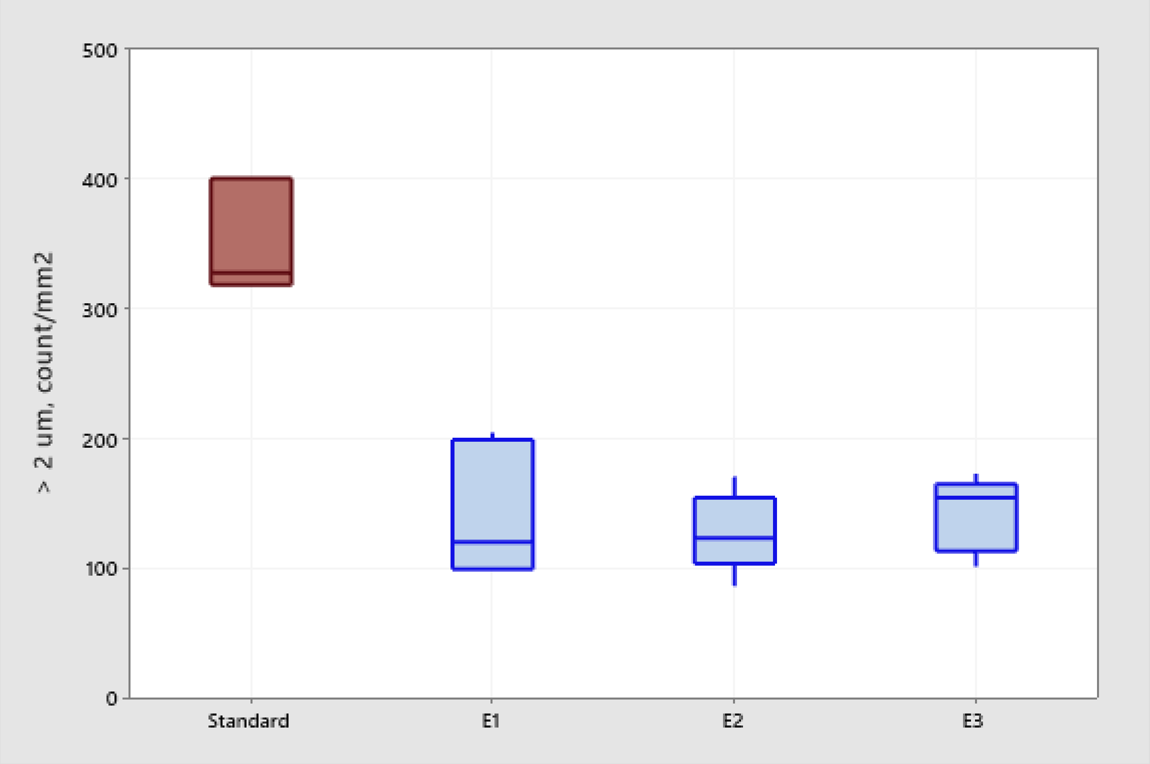
Transverse Inclusions Density

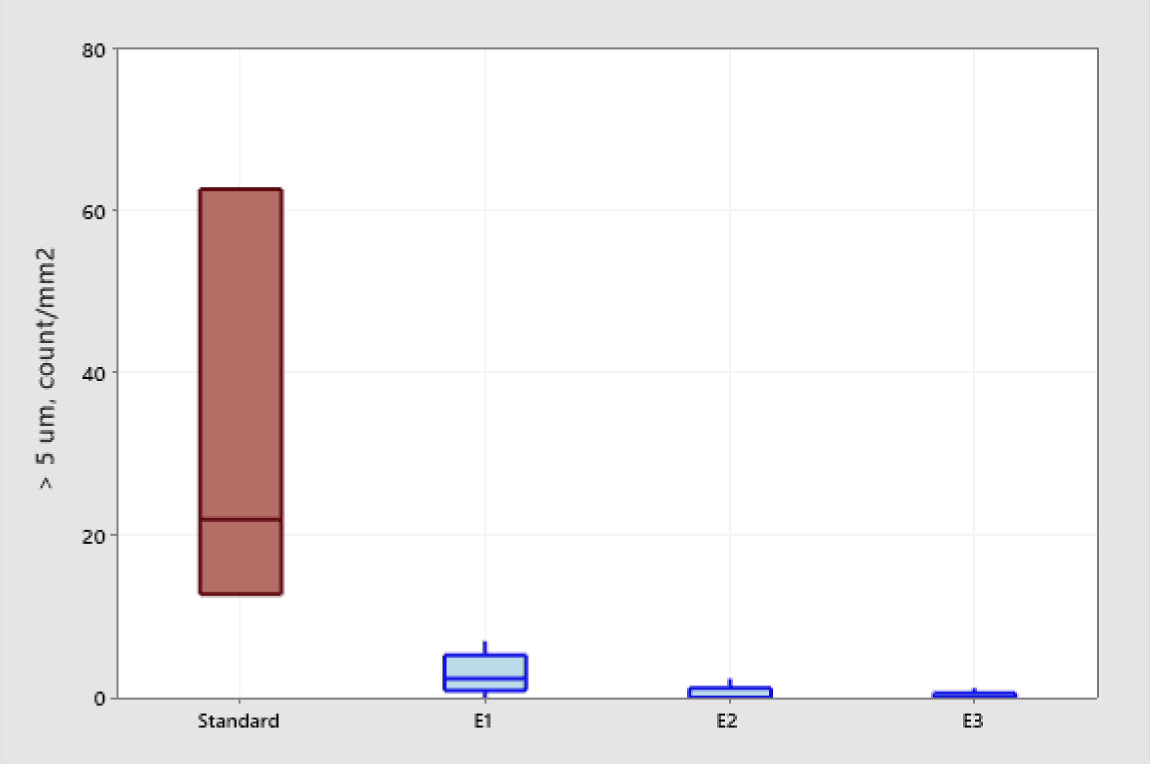
Inclusions > 2 µm

Inclusion density in Enduro has been reduced by ~ 3X

Inclusions > 5 µm

Inclusion density in Enduro has been reduced by ~ 20X





Enduro Characterization Summary

The micro-cleanliness in Enduro material is significantly improved over standard material with good consistency

- Reduced maximum inclusion size and area fraction
- Lowered density of large inclusion particles (>5 µm) by a factor of 10
- Improved micro-cleanliness across entire sections of mill products
- Consistent results within campaigns and across campaigns
- Thermal and mechanical properties are comparable to standard material
- ASTM F2063-18 compliant