ADDITIVE 4 BIOMEDICAL

UNIVERSITÀ DEGLI STUDI FIRENZE
DIEF DIPARTIMENTO DI INGEGNERIA INDUSTRIALE

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MICROSTRUCTURAL AND MECHANICAL CHARACTERIZATION OF NITINOL STENTS PRODUCED BY LASER POWDER BED FUSION BEFORE AND AFTER HEAT TREATMENT

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SC 09/A3 CoCo AM Additive Manufacturing
ASSOCIAZIONE NAZIONALE DISEGNO E METODI
COMET
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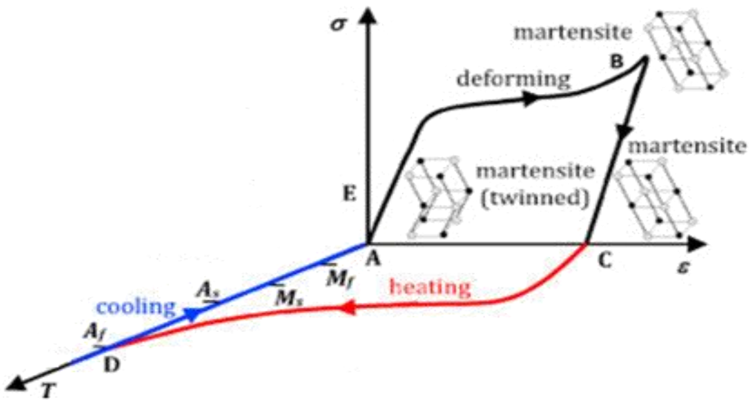
NITINOL (NI-TI)

- Near-equiatomic nichel-titanium alloy, the most common **shape memory metal material**
- **Two different phases** depending on T which determine **two different behaviors**:

SHAPE MEMORY EFFECT



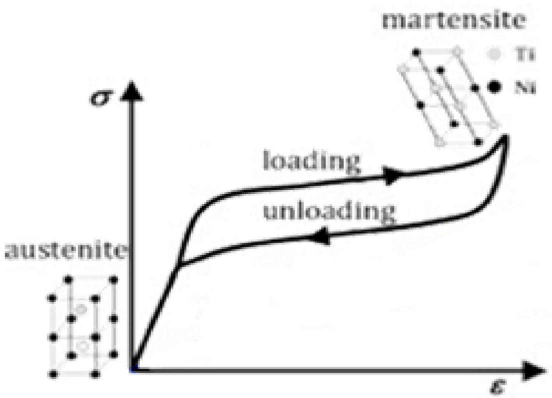
Martensite

$M_f > T_{operation}$

> %Ti

Temperature sensors, actuators…

SUPERELASTICITY



Austenite

$A_f < T_{operation}$

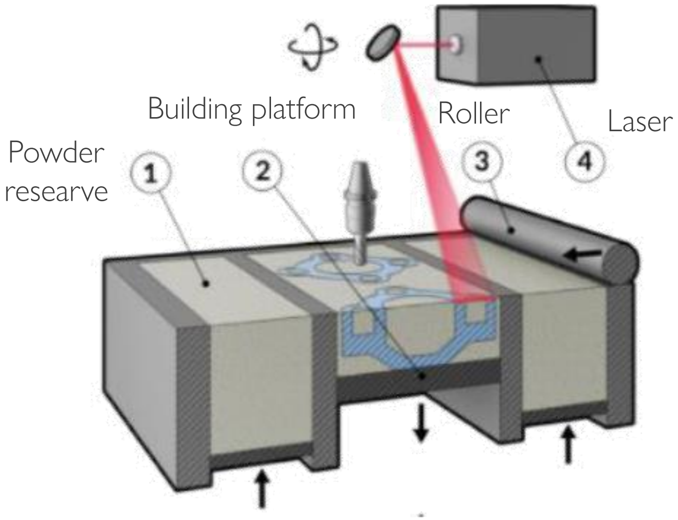
> %Ni

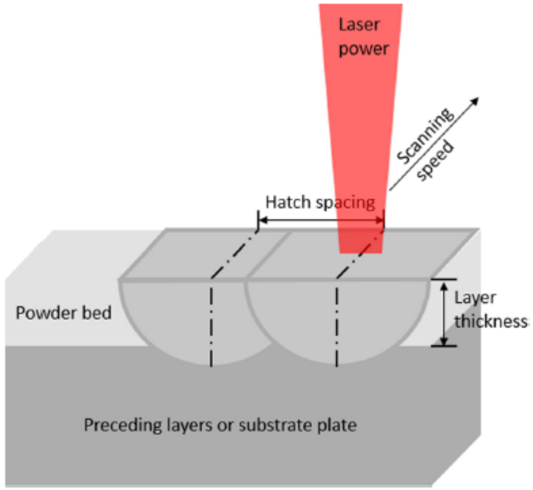
Biomedical implants: stents, filters, orthopedic implants…

Transformation Temperatures (TTs): M_f, M_s, A_s, A_f — T

Laser Powder Bed Fusion (L-PBF)

➢ **Additive manufacturing** tecnique which consists in manufacturing components by adding material **layer by layer**





➢ In the biomedical field:

✓ Advantages	✖ Limits
Freedom of design	Process **complexity**
Possibility to manufacture **tailor-made biomedical implants with complex shape**	Wide number of **parameters** difficult to handle
Lower **costs**	Typical **process defects**

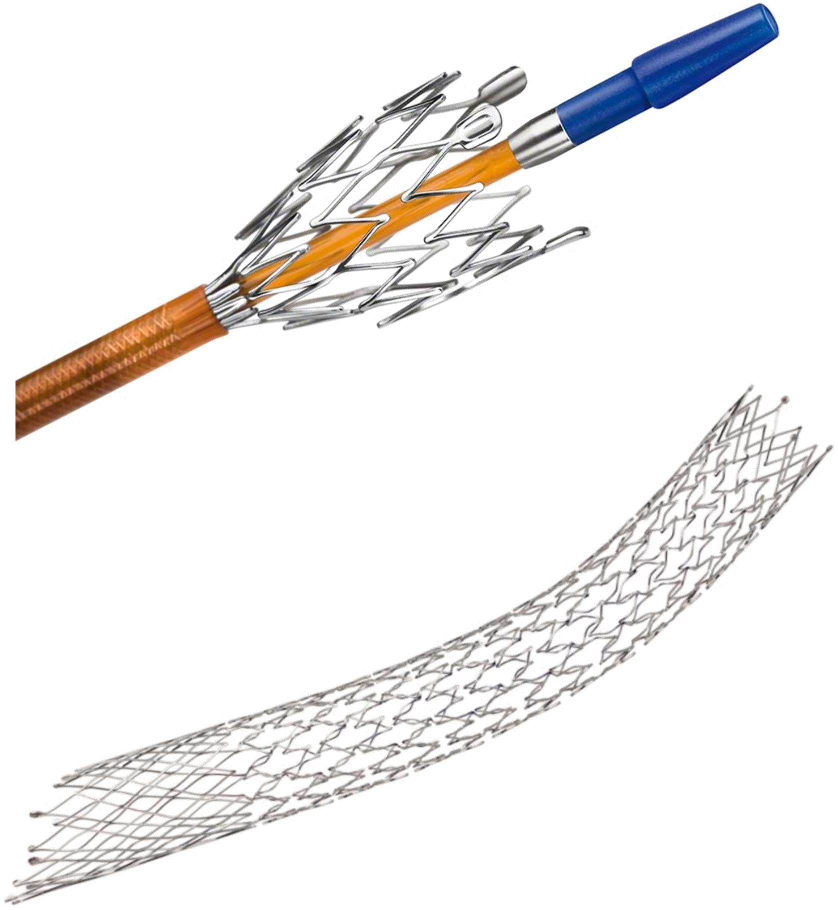
➢ For Nitinol:

- **Ni evaporation** during laser processing
- Formation of **secondary phases**

→ **Temperature transformation** control

→ Obtainment of the superelasticity

Aim of the Work



Investigate the possibility to use **additive manufacturing** techniques to produce **self-expandable stents** in **Nitinol**

Process feasibility
Parameters
Nichel evaporation

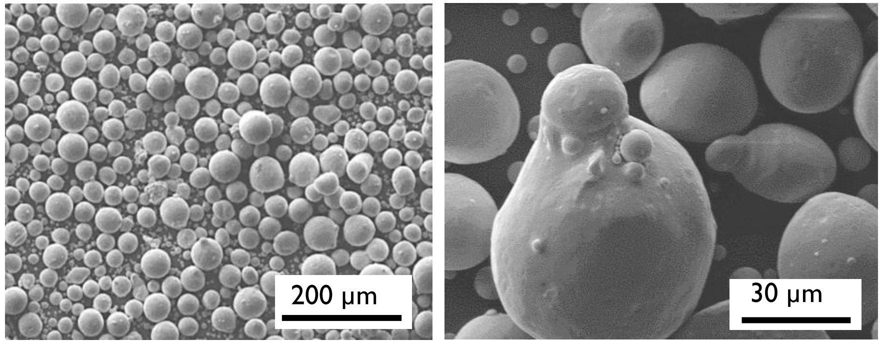
Resulting properties
Transformation Temperatures
Microstructure
Mechanical properties

Overcome the limits of the <u>standardized</u> conventional production

Experimental procedure

➢ **Production**

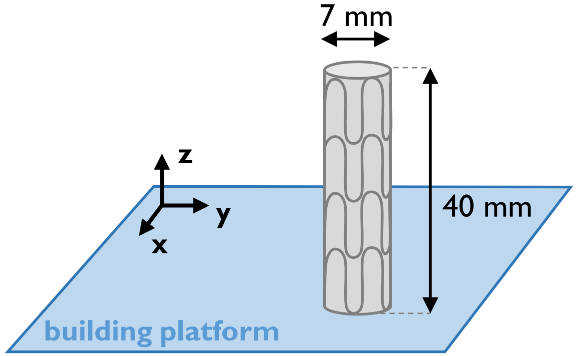
Nitinol powder (%at)	
Ni	Ti
50.54	49.46



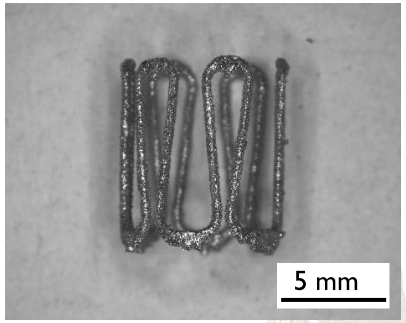
10-70 µm

Laser powder bed fusion			
Sample	Laser Power	Scan Speed	Hatch Spacing
A	150 W	900 mm/s	55 µm
B	180 W	1200 mm/s	70 µm
C	180 W	900 mm/s	70 µm

Layer thickness = 40 µm Spot size = 40 µm



Cutting



➢ **Heat treatments**

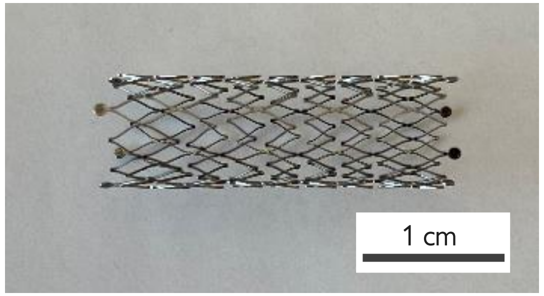
T1	600 °C	1.5 h
T2	1100 °C	1.5 h

- High vacuum
- Argon partial pressure 1 mbar

EXPERIMENTAL PROCEDURE

➢ Conventional stent

- NiTi, self-expandable
- Superficial Femoral Artery Stent (**SFA Stent**)
- Medtronic



➢ Characterization: as-built (A, B, C), T1, T2, SFA stent

Optical microscope
SEM
→ Microstructural characterization

DSC analyses
-90 ÷ 180 °C
10 °C/min
→ Transformation Temperatures (TTs)

Crush tests

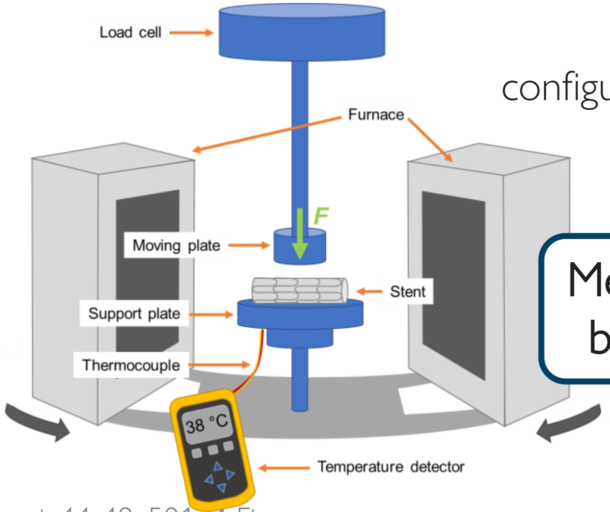
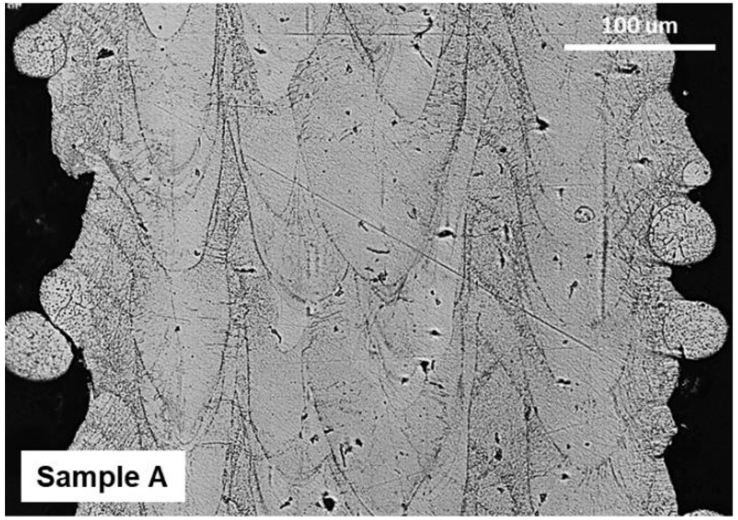
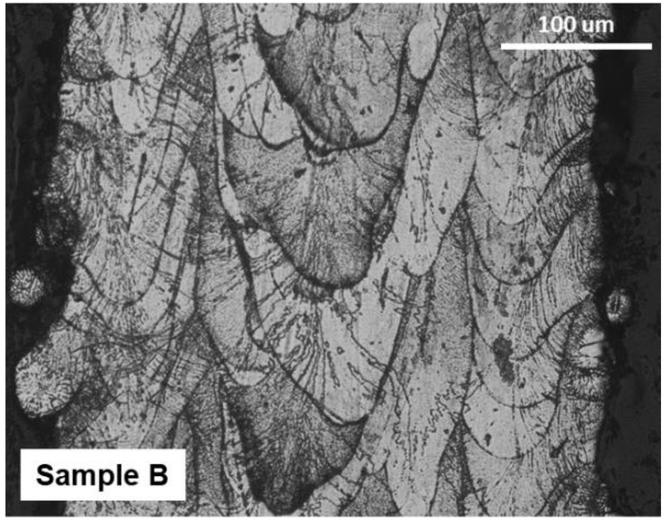


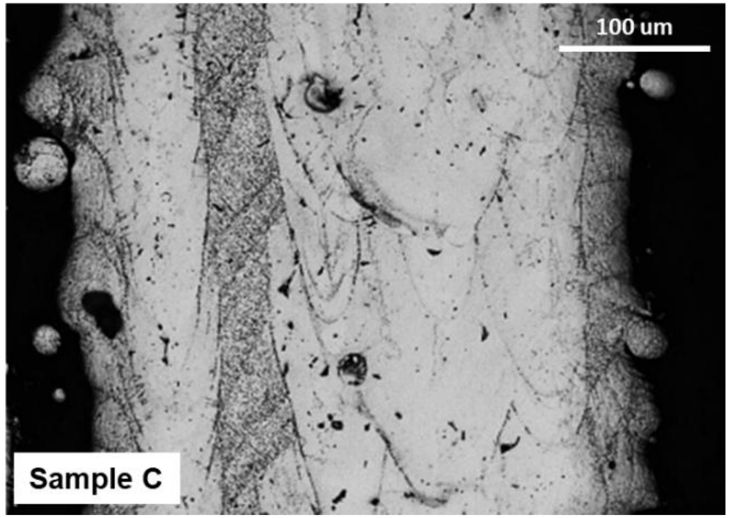
Plate-to-plate configuration, 37 °C
ISO 25539-2

→ Mechanical behavior

RESULTS: AS-BUILT SAMPLES





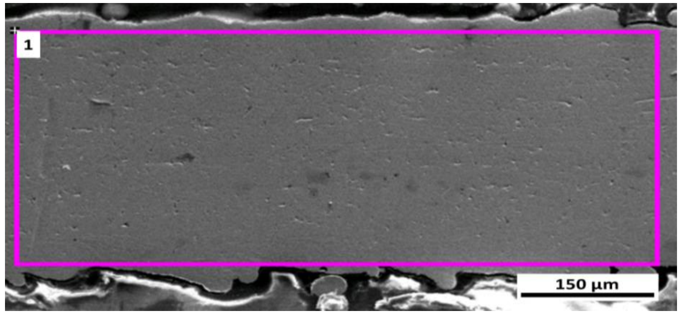


- Melt pools and columnar grains
- Porosities
- Not completely fused particles → poor surface finishing

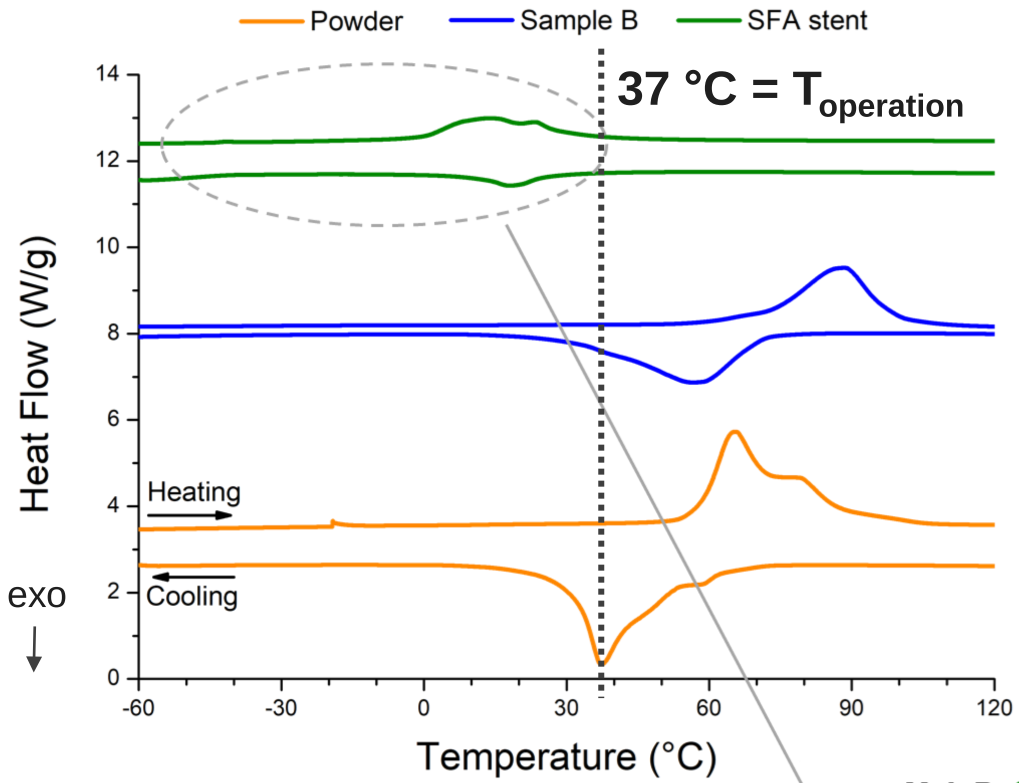
1.5% Ni loss

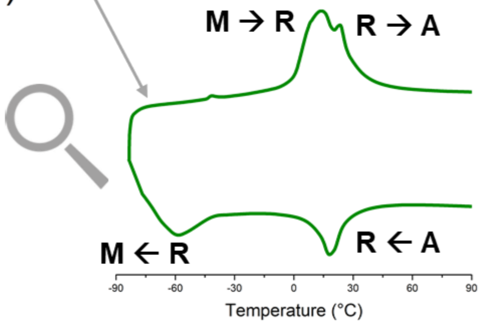
	Ti	Ni
1	51.02	48.98

(at%)



RESULTS: AS-BUILT SAMPLES





SFA stent

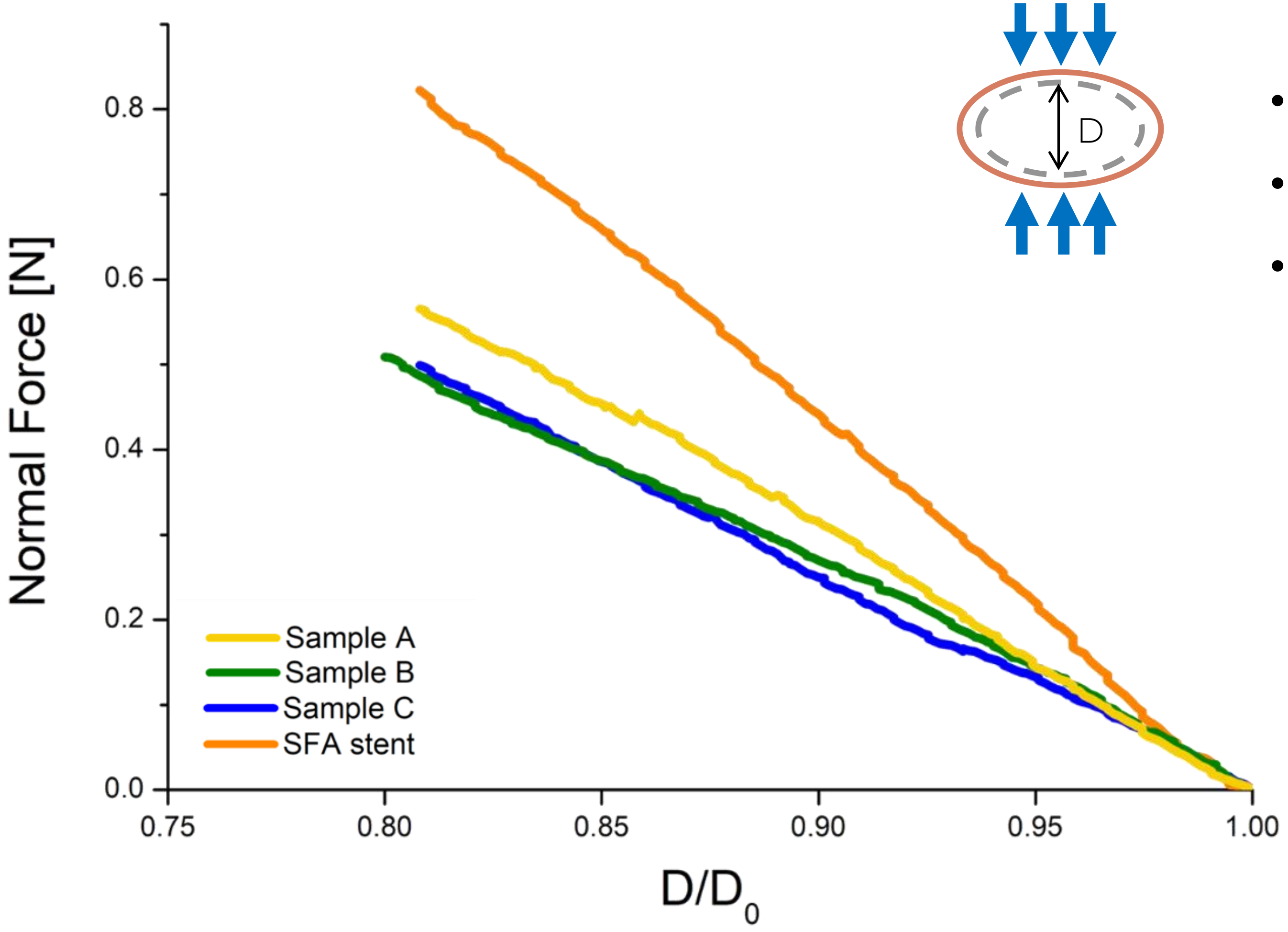
- Double peaks
- $|T_A - T_R| < 10$ °C
- Austenite at $T_{operation}$

→ presence of the **R-phase**

L-PBF samples

- **Equal TTs** in samples A, B, C
- **No double peaks**
- **Martensite** a $T_{operation}$
- Curves **shift to the right** compared to powder → **Ni loss** during the process

RESULTS: AS-BUILT SAMPLES

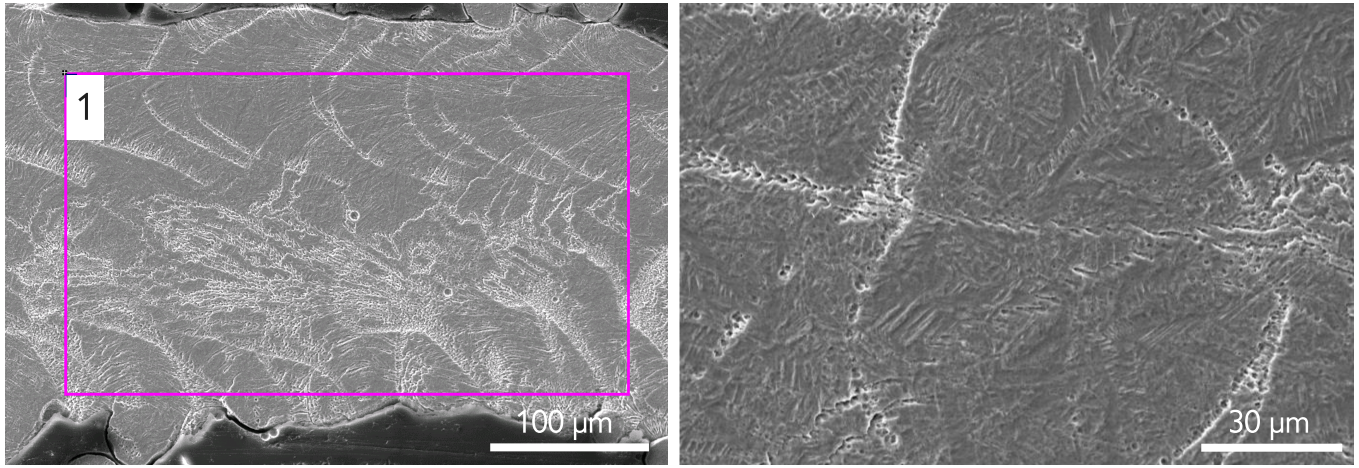


- **Almost linear** behaviour
- **Negligible** effect of the **process parameters**
- **Lower compressive strength** of L-PBF stents compared to SFA stents

Compression resistance (N)	
Sample A	0. 70 ± 0.19
Sample B	0.51 ± 0.07
Sample C	0.45 ± 0.07
SFA stent	0.82 ± 0.03

RESULTS: HEAT-TREATED SAMPLES

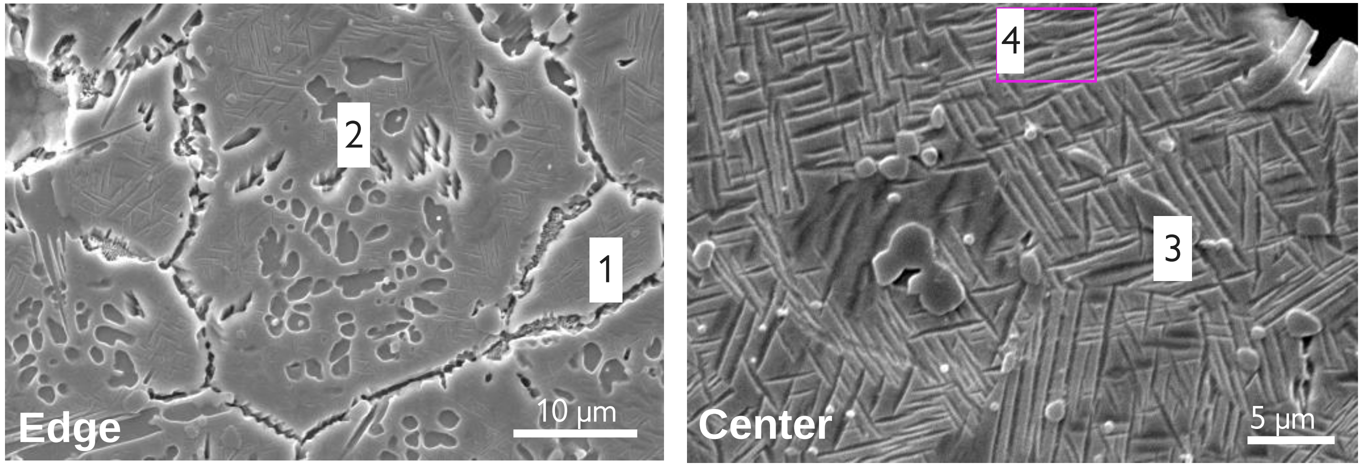
T1



	Ti	Ni
1	50.99	49.07

(at%)

T2



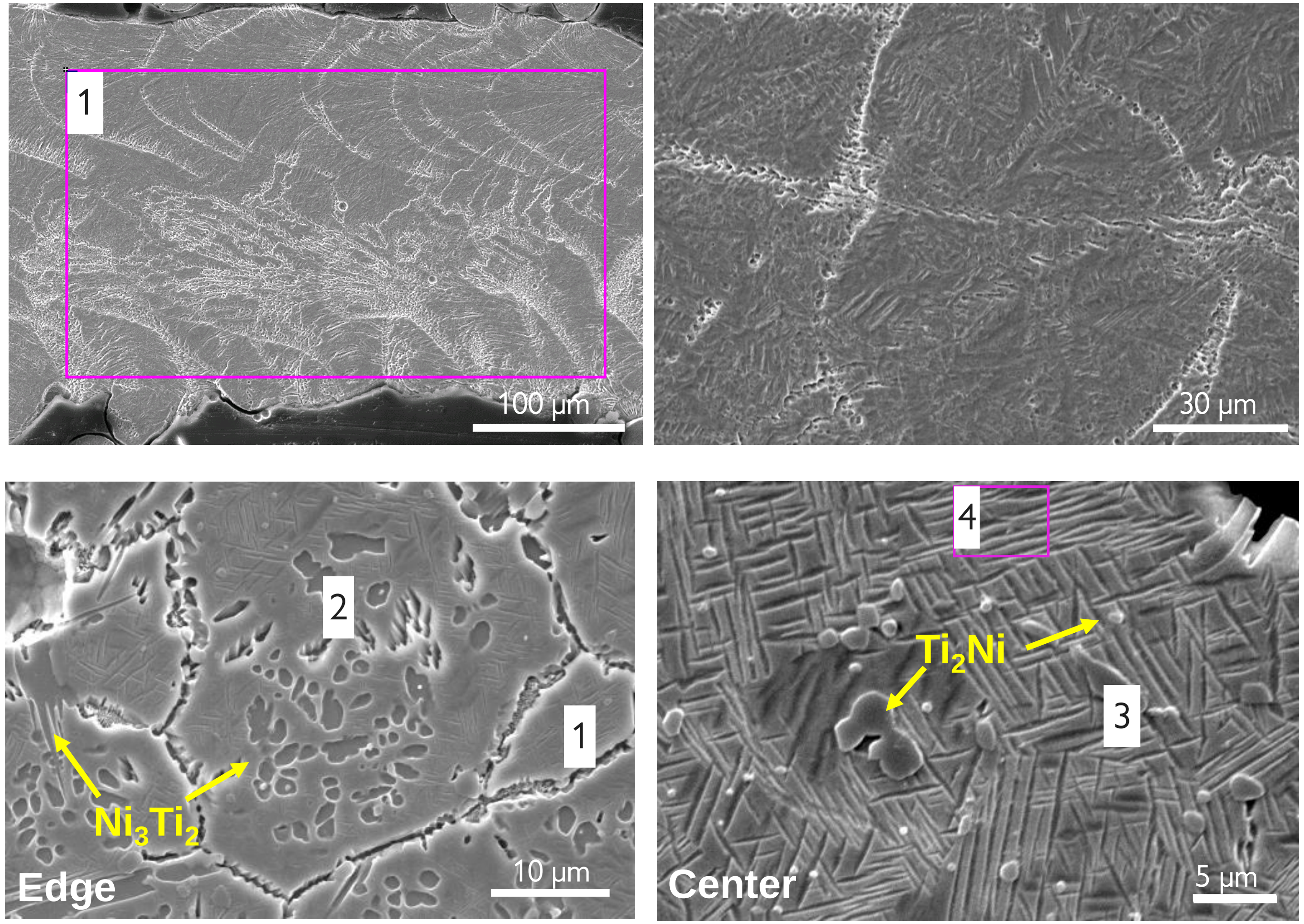
	Ti	Ni	
1	49.49	50.51	→ matrix
2	41.86	58.14	→ Ni-rich
3	63.84	36.16	→ Ti-rich
4	48.23	51.77	→ matrix

(at%)

RESULTS: HEAT-TREATED SAMPLES

T1

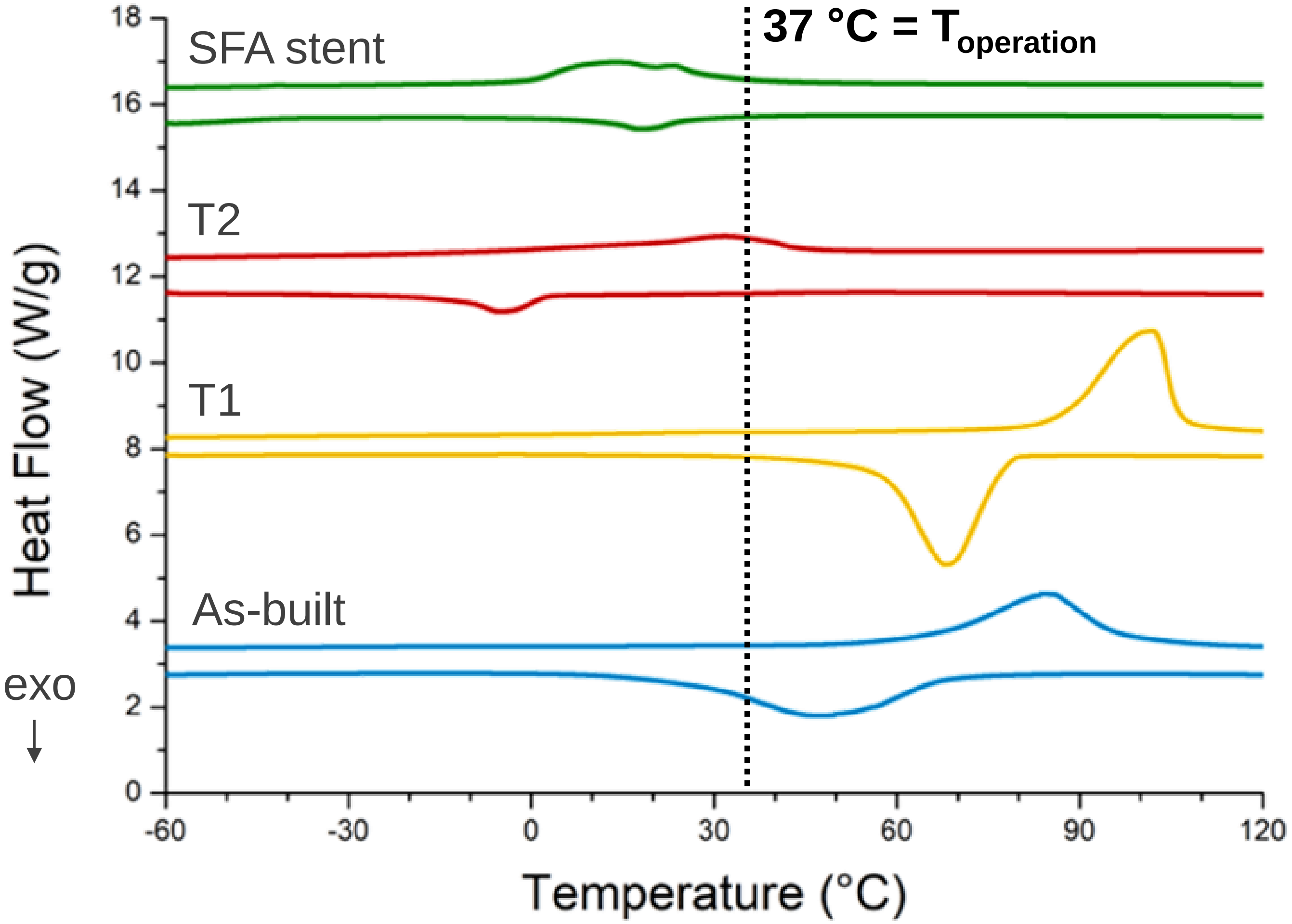
T2



- Permanence of the **L-PBF structure**
- **Martensite** phase within the melt pools

- **Mixed structure**: austenite near the edges, martensite at the center
- **Ti_2Ni phase** formation
- **Nichel rich precipitates** (≈Ni_3Ti_2) as result of the matrix chemical variation

RESULTS: HEAT-TREATED SAMPLES



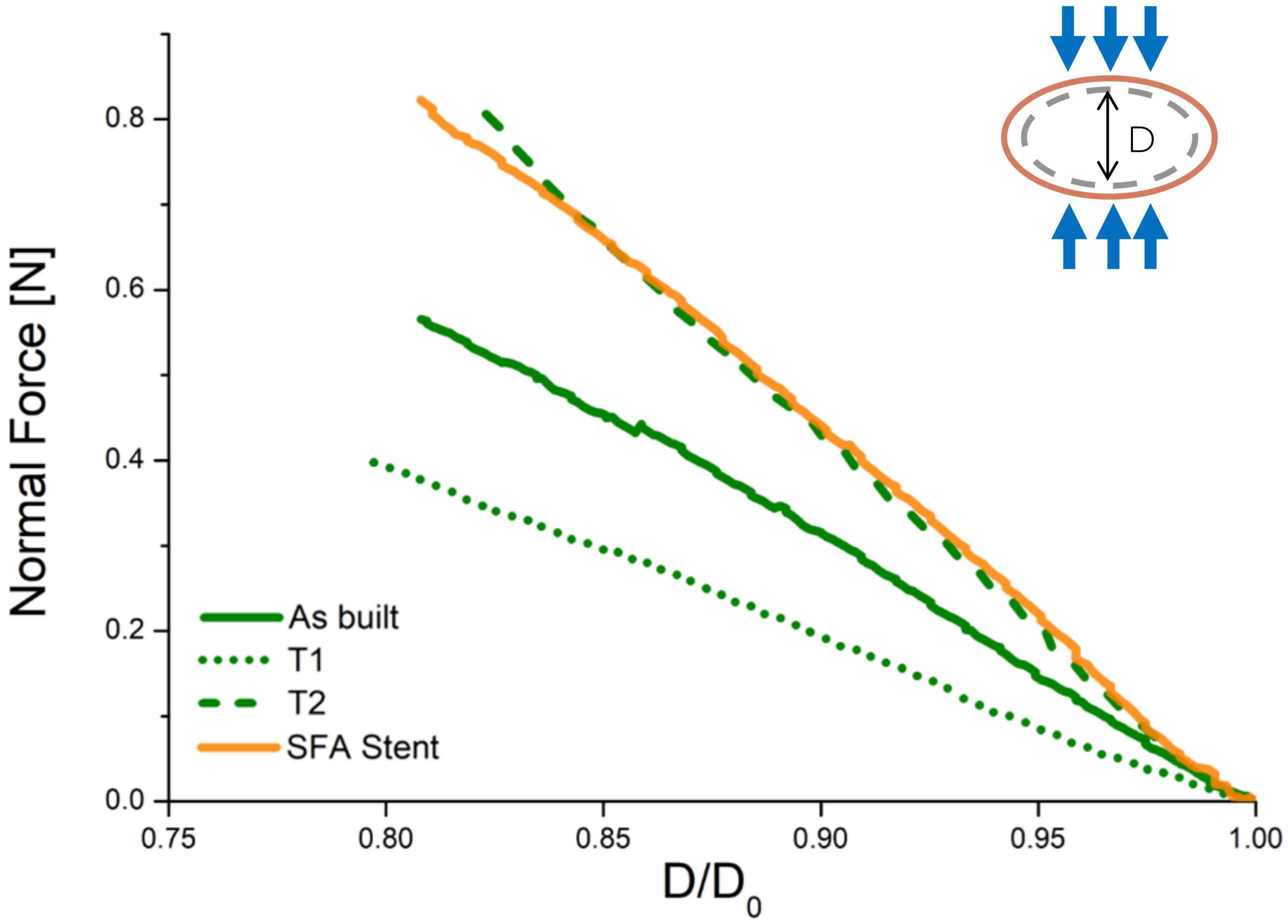
T1

- Slight shift to the **right** (+20 °C)
- More evident peaks → more homogeneous structure
- Martensite at $T_{operation}$

T2

- Shift to the **left** (-60 °C)
- More rounded peaks → more heterogeneous structure
- Mixed structure at $T_{operation}$
- Curves closer to those of SFA stent

RESULTS: HEAT-TREATED SAMPLES



- T1 worsens resistance
- T2 improves resistance → similar behaviour to SFA stent

Compression resistance (N)	
L-PBF stent	0. 70 ± 0.19
T1	0.41 ± 0.01
T2	0.82 ± 0.03
SFA stent	0.82 ± 0.03

Conclusions

As-built

- **1.5% Nichel loss** during the process
- **L-PBF** stents exhibit the **same overall behaviour**

→

Next developments

- Changing the **process parameters**
- Changing the **powder chemical composition**

Nitinol powder (%at)	
Ni	**Ti**
52.39	47.61

Heat-treated

- **T1** (600 °C, 1.5 h) → **stress relieving**
- **T2** (1100 °C, 1.5 h) → change in microstructure, which approaches the ideal one for **superelasticity**

→ **properties close to those of the conventional stent**

Heat treatments can constitute an operative method to shape the alloy to achieve the desired properties, but which in any case cannot disregard from an effective process control

Thanks for the attention

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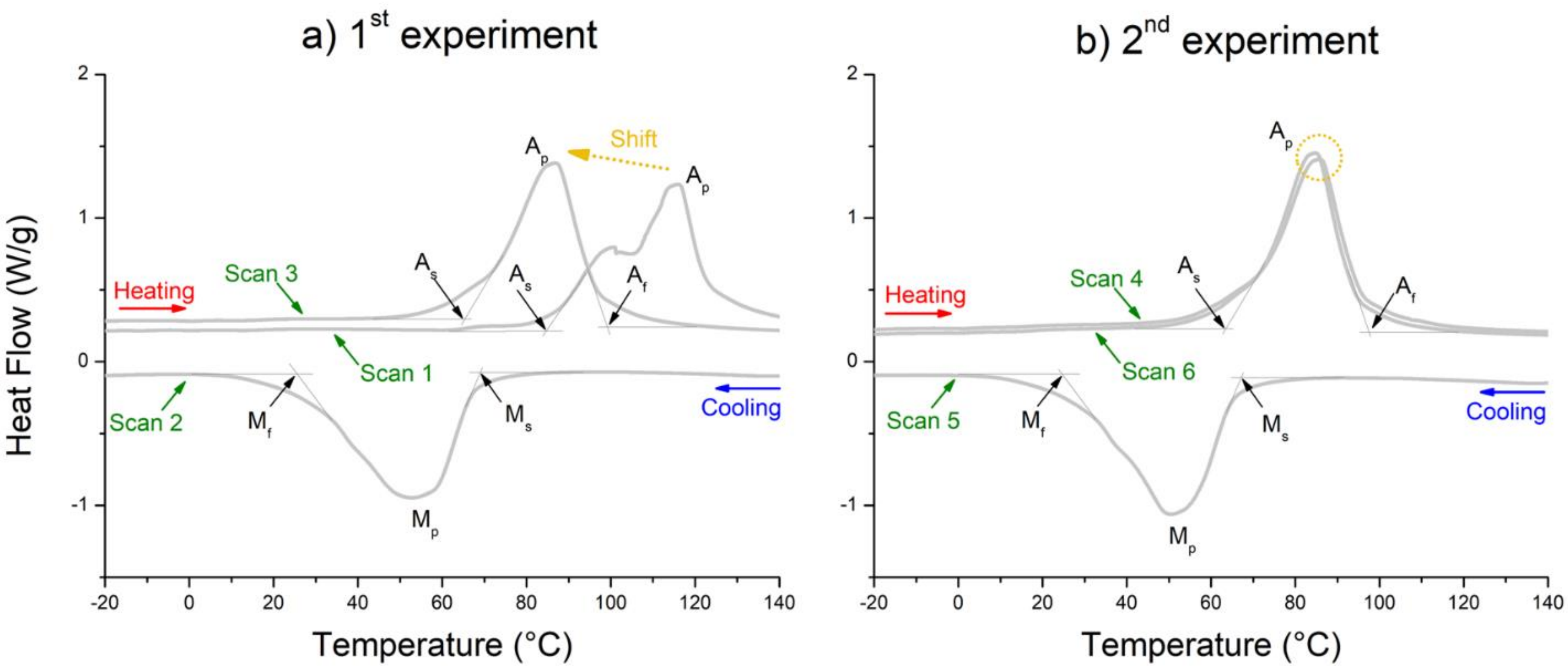
TTs

Material	Temperature (°C)								
	M_f	M_p	M_s	R_f	R_p	R_s	A_s	A_p	A_f
Powder	31	37	49	-	-	-	58	66	77
Sample A	28	53	68	-	-	-	69	87	93
Sample B	35	57	86	-	-	-	71	88	98
Sample C	28	47	68	-	-	-	65	84	97
SFA stent	<-70	-60	-40	10	18	27	19	23	31

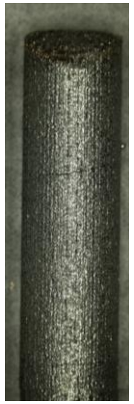
Material	Temperature (°C)								
	M_f	M_p	M_s	R_f	R_p	R_s	A_s	A_p	A_f
As built	28	47	68	-	-	-	65	84	97
T1	58	68	78	-	-	-	86	102	106
T2	-13	-5	3	-	-	-	-17	32	45
SFA stent	<-70	-60	-40	10	18	27	-1	14	31

TTs



a) 1st experiment
b) 2nd experiment
Heat Flow (W/g)
Temperature (°C)
Heating
Cooling
Scan 1
Scan 2
Scan 3
Scan 4
Scan 5
Scan 6
Shift
A_p
A_s
A_f
M_s
M_f
M_p

Next developments

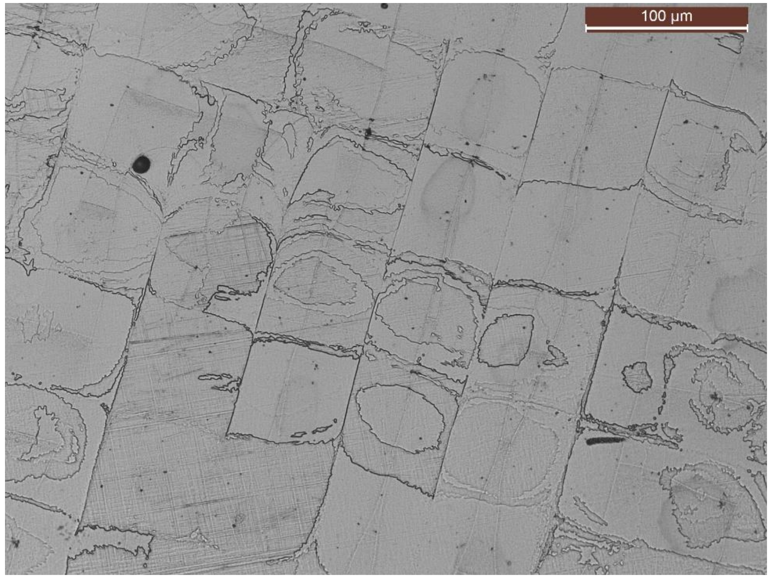


Nitinol powder (%at)	
Ni	Ti
52.39	47.61

Sample	Laser Power	Scan Speed	Hatch Space
S2	150 W	500 mm/s	80 µm
S3	180 W	1000 mm/s	80 µm
S4	180 W	500 mm/s	80 µm

Layer thickness = 60 µm
Spot size = 60 µm

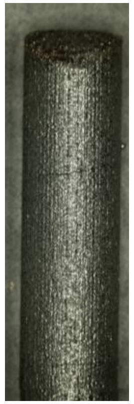
xy, 200X



z, 100X

z, 200X

Next developments



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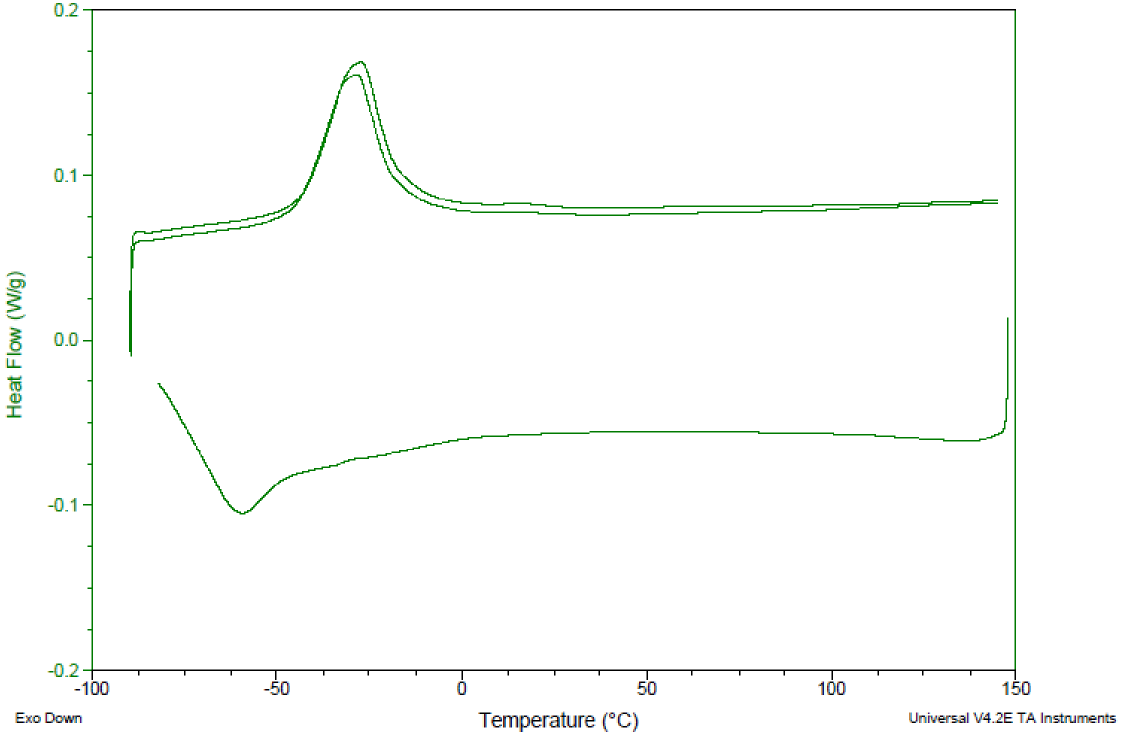

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