ACHIEF

2-Years progress WORKSHOP

BOOSTING HIGH-PERFORMANCE MATERIALS FOR ENERGY INTENSIVE INDUSTRIES

Thursday 1st December 2022
9:30-12:00 CET

Development Of High Entropy Alloys-HEAs- For High Temperature Applications

Dr. Pilar Rey Rodriguez

aimen TECHNOLOGY CENTRE · cea · VTT · Seamthesis · Constellium · ArcelorMittal

The project has received funding from the European Union's Horizon 2020 research and innovation program under Grant Agreement N° 958374.

WP4 Targets

Our main Objective: to develop new HEAs by atomization to be printed using laser based-AM processes to be validated in EIIs test cases

O4.1. To develop innovative HEA materials with improved high-temperature resistance properties (i.e., high-temperature strength and creep) and provide novel protective coatings based on HEA composites allowing high-temperature wear performance of coated components.
O4.2. To develop novel multi-component equiatomic HEA powders suitable for powder based AM process using gas atomization technique.
O4.3. To determine optimum process conditions for laser-based additive manufacturing of HEA materials
O4.4. To correlate HEAs´ composition and powder characteristics to their microstructure and properties attained by means of laser-based manufacturing processes, feeding and closing the loop with WP2

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[1] Fibre Optic Sensors
[2] Laser based Powder Bed Fusion
[3] Laser Based Directed Energy Deposition
[4] ThermoCalc
[5] Density Functional Theory
[4] Mechanical Alloying
[5] Laser Cladding

WP4 in ACHIEF Value Chain

engionic Fiber Optics — WP6: Sensing: FOS[1] (T & strain) — aimen Technology Centre

WP2: Digital Tools

WP4: Materials & Processes

WP7 & 8: Pilot test assesment & exploitation

aimen — AI
+
VTT — Modelling TC[4]+DFT[5]

VTT — Atomized HEAs for coating & bulk

Seamthesis

HEA selected from SOA for benchmarking

cea — LPBF[2]

aimen — DED-LB[3]

aimen — MA[6]+ LC[7]

Re-heating furnace SLABS

HT strength and creep resistance

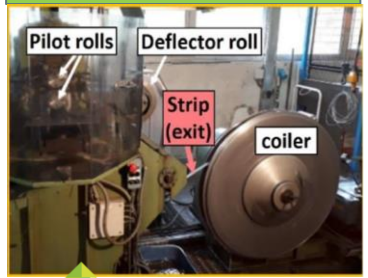
STEEL

ArcelorMittal

Roll MMCs COATINGS

HT WEAR resistance

ALUMINIUM



Constellium

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WP4: Materials

Materials objective: good quality with high temperature properties (tensile and creep resistance for AM and wear for LC)

SoA-HESA: Ni58,2Al10Co13,8Cr6,3Fe4,9Ti6,8

High Entropy Super alloy

OBJECTIVE:

To promote high rate of hardening γ ' phase in a γ matrix, looking for higher volume fraction and diametre of γ '

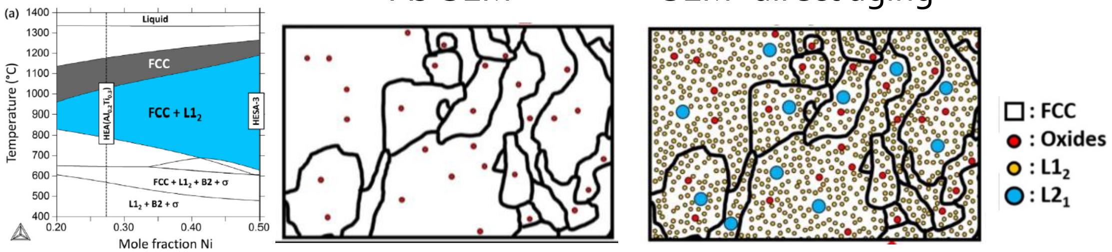
Al-MEA: Ni28,6Fe28,6Co28,6Al14,3

Medium Entropy complex concentrated alloy

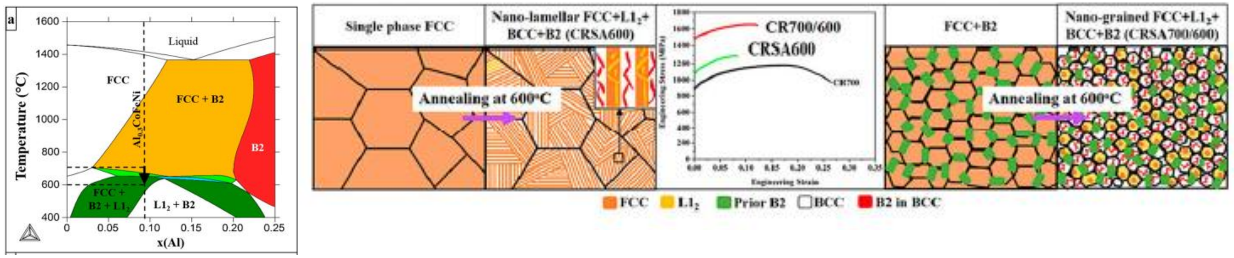
OBJECTIVE:

Promoting multi-scale microstructure of fine scale FCC+LI2 grains mixed with B2+BCCgrains

As-SLM SLM+direct aging



Wei-Chih Lin, et al., Additive Manufacturing, 36, 2020, 101601



S. Dasari et al., Mater. Res. Lett., 2020, VOL. 8, NO. 11, 399–407

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HEAs atomization

To atomize the lab powder batches the steps below were followed

I. Preparing of the pre-alloy

- Melting/Solidifying the alloy several times to homogenize
- Induction heating for melting the pre-alloy and crucible solidification
- Solidified ingot sectioning to be leaded in the atomization crucible

II. Atomization of batches of 15 kg at VTT with Hermiga 75/5VI gas atomizer

- The pre-alloy batches were heated to melting temperature and over heated to ensure free flow of the melt stream
- The melt was fed through aluminium oxide nozzle and the melt stream was atomized with high-pressure in argon gas. The powder was then left to cool inside the atomization chamber in argon to avoid oxidation
- Two fractions were produced:

a) Chamber fraction: the main fraction, was sieved into suitable Particle Size Distribution (PSD), for LPBF (<45µm) & DED-LB (+45 – 125µm)

b) Cyclone fraction is very fine, so unusable for AM

Source: VTT atomizer

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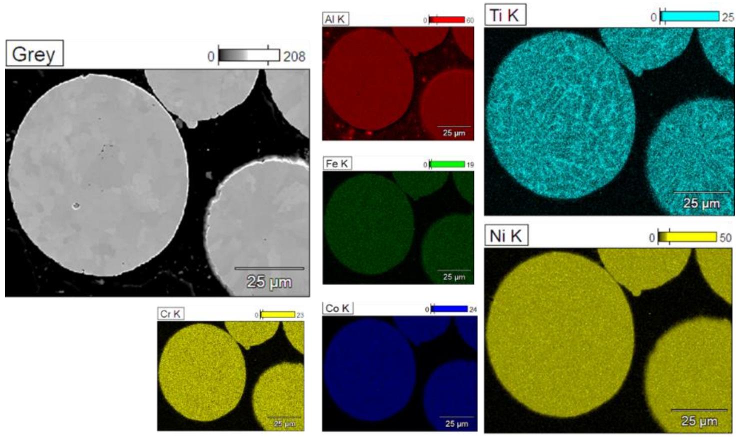
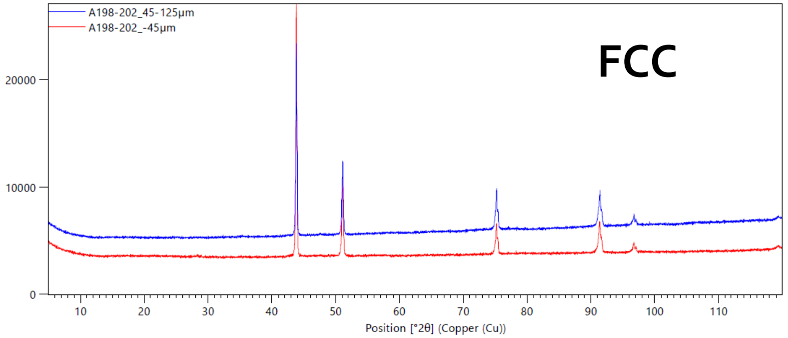
Chemical and crystalline powder analysis: Energy-dispersive X-ray spectroscopy (EDS) &X-Ray Diffraction (XRD)

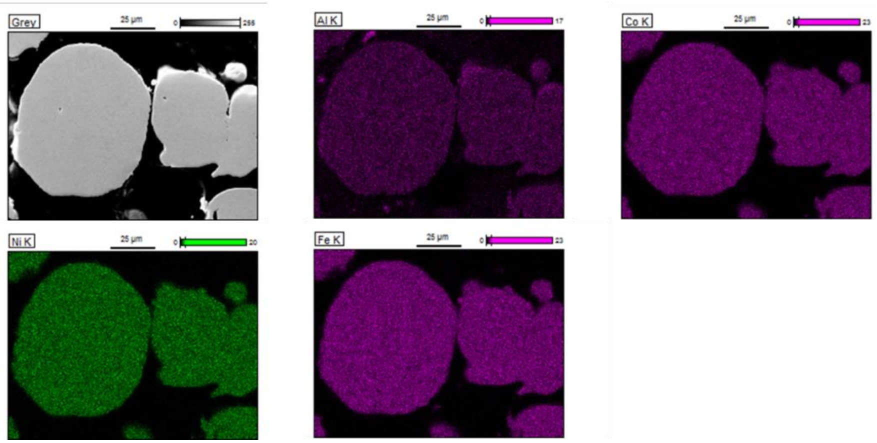
- -Got <1at-% accuracy for the final composition
- Ti segregation in inter-dendritic regions in SoA-HESA
- No element segregation observed in AI-MEA

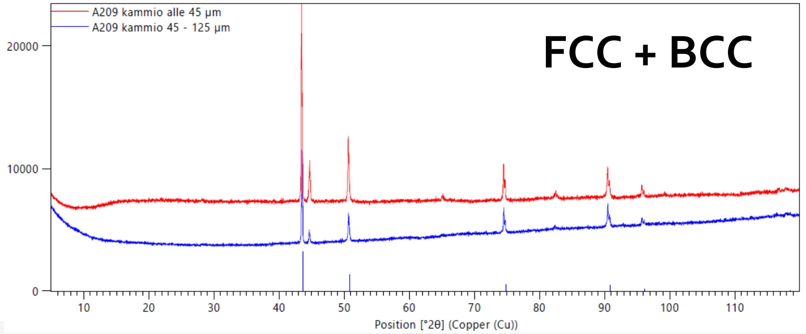
SoA-HESA





AI-MEA





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WP4: Materials

Thermal behaviour powder analysis: Differential Thermal Analysis (DTA)

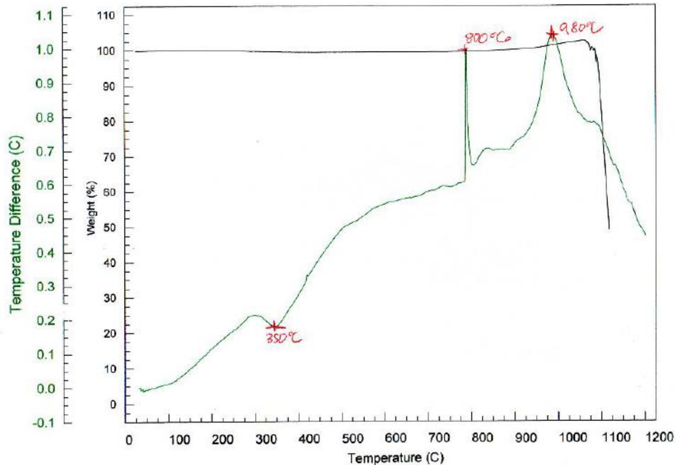
- In air, 1 exo peak at 800ºC (phase transformation) and 980ºC (exo) that is associated with a great loss of weight (oxidation & evaporation)
- In Ar, defined peaks disappear, but still weight loss is observed with violent oscillations

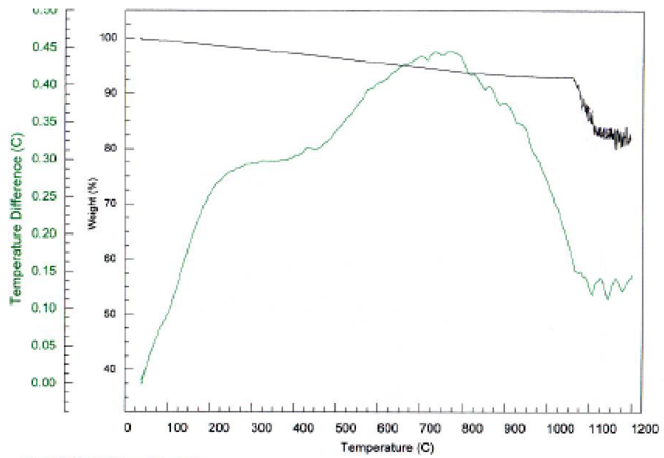
- In air, three peaks (exo) with weight gain probably due to oxidation
- In Ar, defined peaks disappear, and weight changes are almost neglectable

AIR

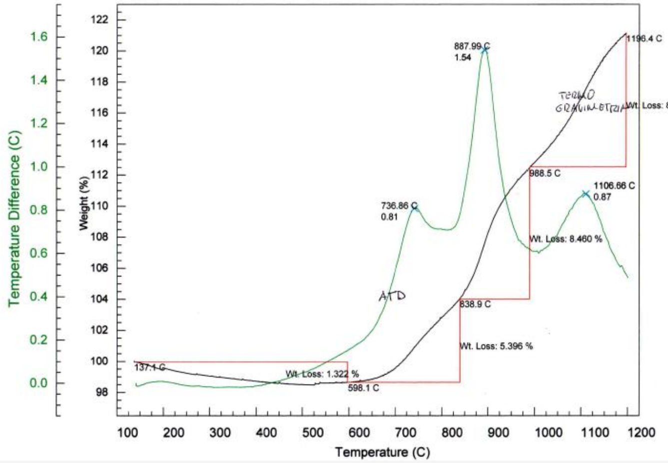
ARGON

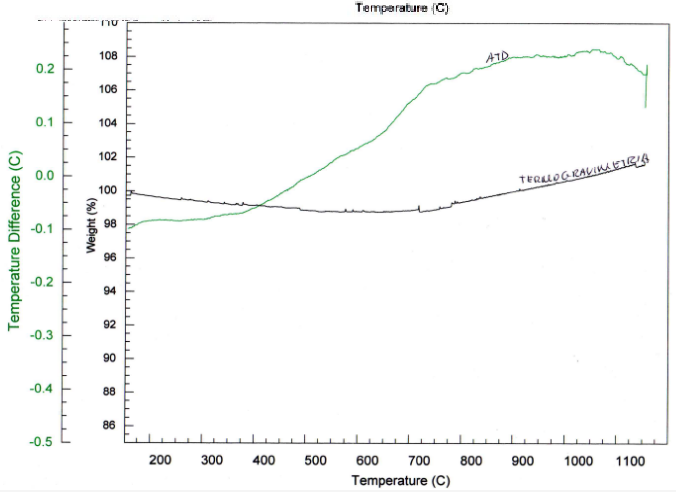
SoA-HESA





AI-MEA





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WP4: Materials

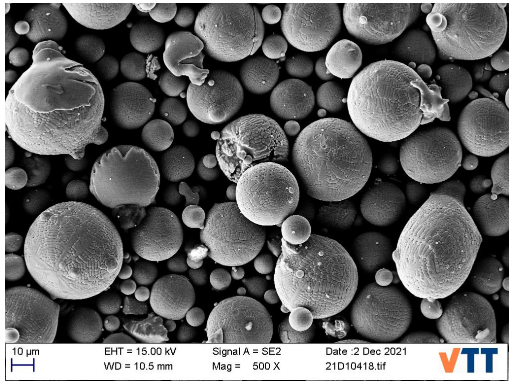
Powder morpholyg and Particle Size Distribution: Scanning Electron Microscopy (SEM) & Laser Diffraction

- Typical gas atomized powder spherical morphology is shown
- Satellite formation avoided
- PSD homogeneous

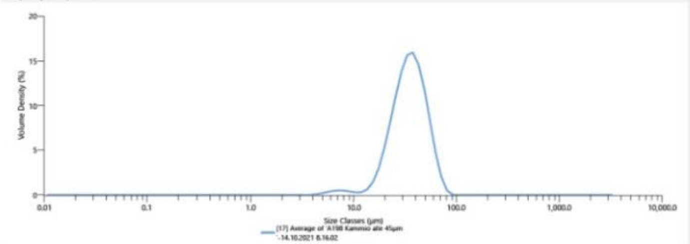
SoA-HESA

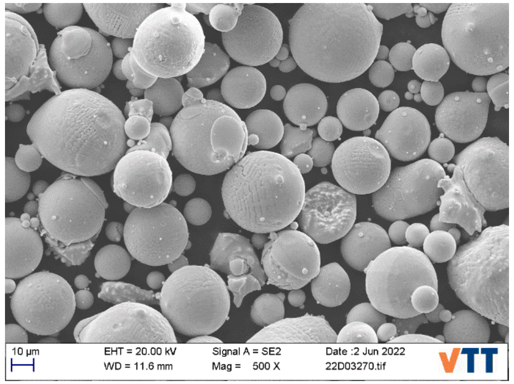
AI-MEA

LPBF

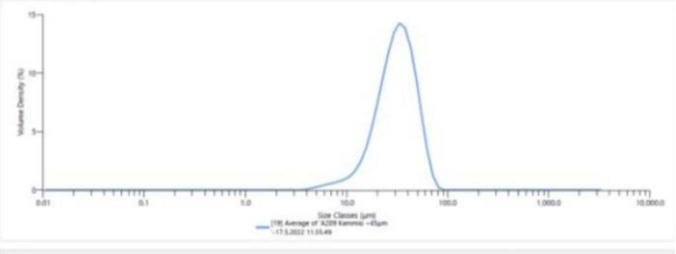


20-55µm (d10-d90)

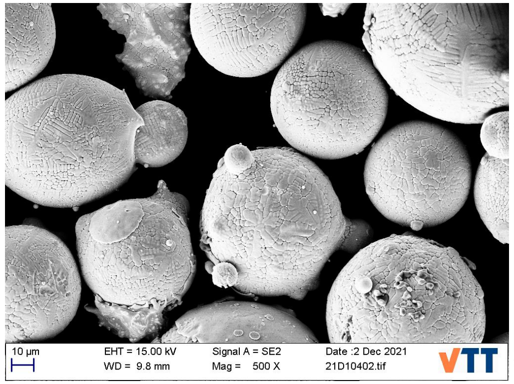




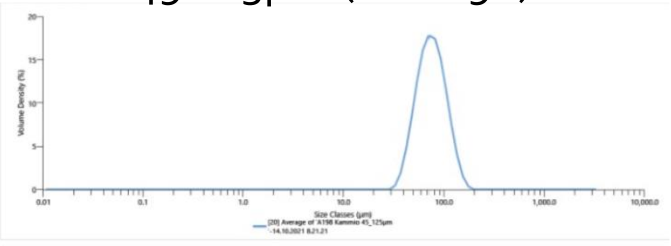
16-51µm (d10-d90)

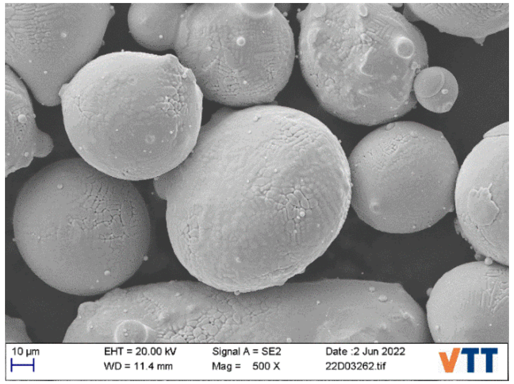


DED-LB

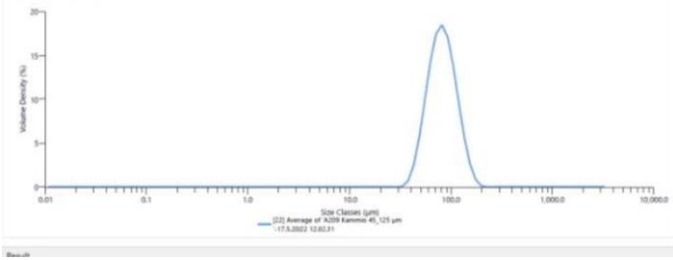


49-113µm (d10-d90)





54-122µm (d10-d90)



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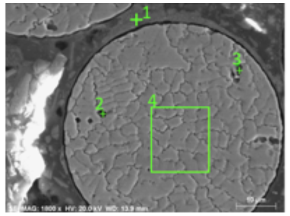
WP4: Materials

HEAs mixing: HEAs based MMCs

- ❑ Mixes prepared in Turbula mixer
- ❑ BPR with YSZ balls 1:1 used
- ❑ 24h mixing
- ❑ Different ratios and type of reinforcement

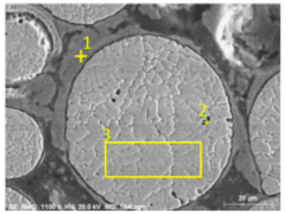
- ✓ After mixing, particles remained almost spherical
- ✓ EDS analysis confirmed that the n-TiC remains in the outer part of HESA1 particles forming like a shell

Sample	Hall Flow	Nº measurements for reproducibility	Tap(yes/no)
HESA1	17,9	6	
HESA1HESA1+ 4%vol. n-TiC	19,2	5	
HESA1HESA1+ 8,5%vol. n-TiC	20,7	13	Yes (occasionally)
HESA1HESA1+ 15%vol. n-TiC	24,0	14	Yes (all measurements)



Mass percent (%)

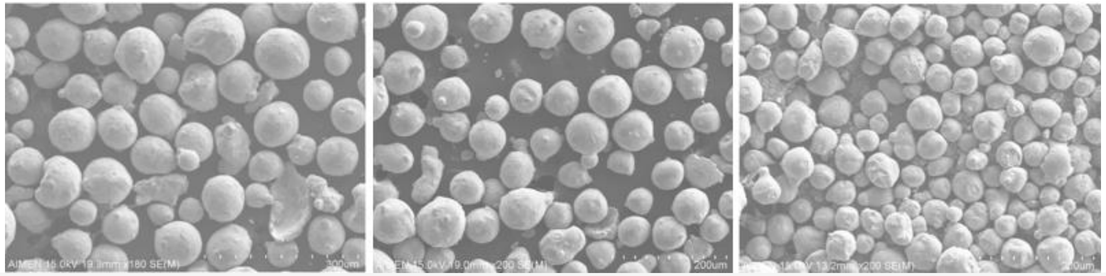
Spectrum	C	O	Al	Si	Ti	Cr	Fe	Co	Ni
1	23.26	9.93	3.26	0.09	61.74	0.00	0.00	0.33	1.38
2	1.70	0.13	2.75	11.58	3.91	5.89	2.93	14.39	56.72
3	4.12	0.36	2.76	1.41	3.04	5.99	2.80	16.78	62.73
4	7.35	1.00	5.40	0.11	3.78	5.76	2.57	14.68	59.35



Mass percent (%)

Spectrum	C	O	Al	Si	Ti	Cr	Fe	Co	Ni
1	26.23	9.74	1.17	0.00	61.81	0.00	0.00	0.00	1.05
2	11.59	0.78	4.42	0.23	3.04	6.18	2.58	14.88	56.30
3	5.04	0.61	4.44	0.02	3.81	5.84	3.01	15.45	61.79

EDS analysis on the cross section of a SEM micrograph on a 4%voln-TiC/HESA1 (top) & 15%vol n-TiC/HESA1 particles (bottom)



SEM micrographs of pre-alloyed batches of HESA1 with 4, 8.5 and 15%vol. n-TiC from the left to the right showing size and shape of the particles.

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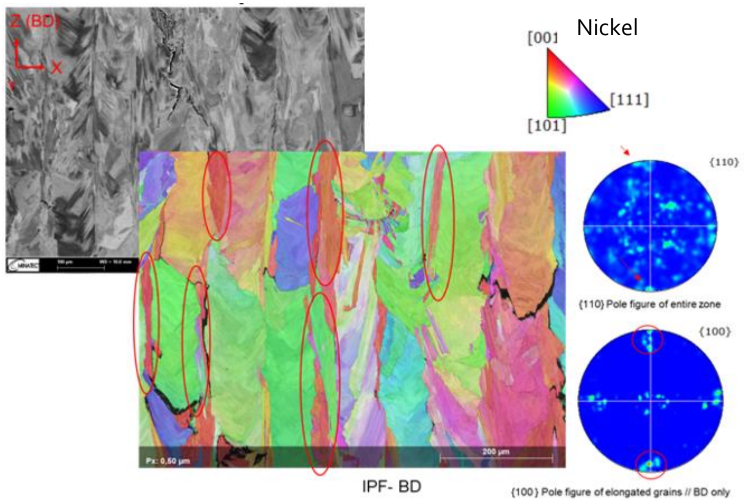
WP4: Processes

Laser Based Powder Bed Fusion (LPBF)- SoA HESA

MAIN RESULTS:

- LPBF conditions allow to obtain parts with **99.2-100%** relative density
- A network of cracks detected by µCT and OM; surface crack density evaluated: 3.6 mm/mm²
- Cracks at the High Angle Grain Boundaries, following the solidification cells joints.

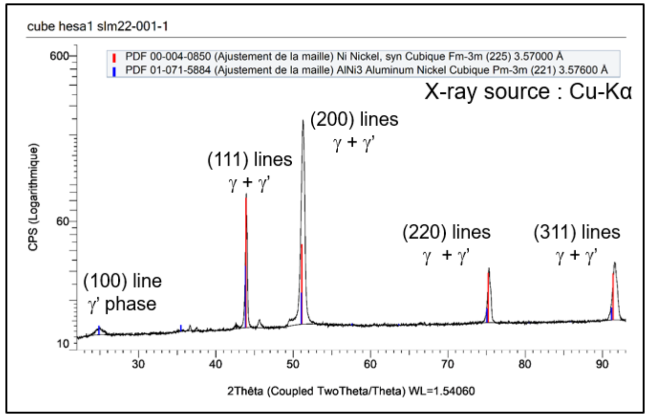
LPBF samples on their baseplate

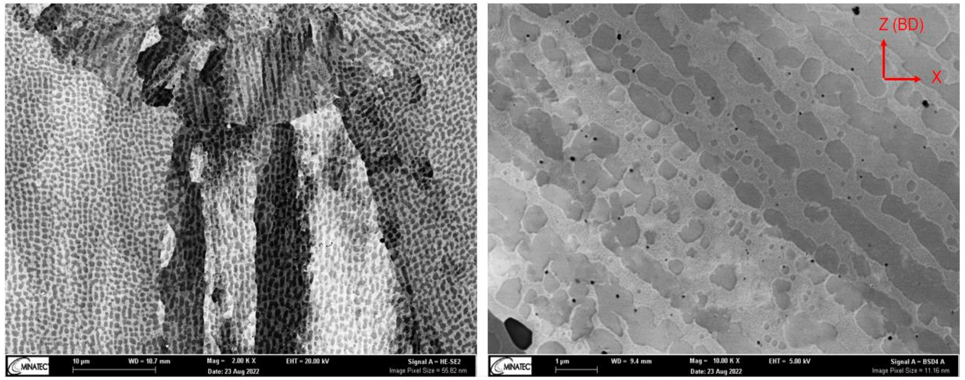


SEM-BSE image and ESBD maps in plane XZ

- **Presence of γ et γ ' confirmed by XRD**; Fraction of 42% of γ ' phase **consistent with predictions**; γ' nano-precipitates of size < 5 nm detected by TEM
- After solution annealing + precipitation hardening , γ' precipitates, spherically shaped and enriched in Al, Ti and Ni have significantly increased and represent 50% of the surface

ϑ-2ϑ XRD on top surface of a LPBF cube





Duplex γ/γ' microstructure after heat treatment (SEM)

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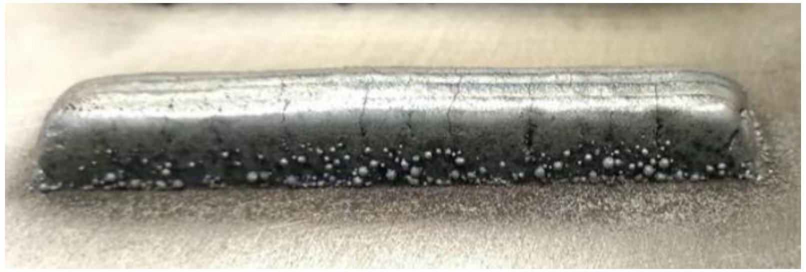
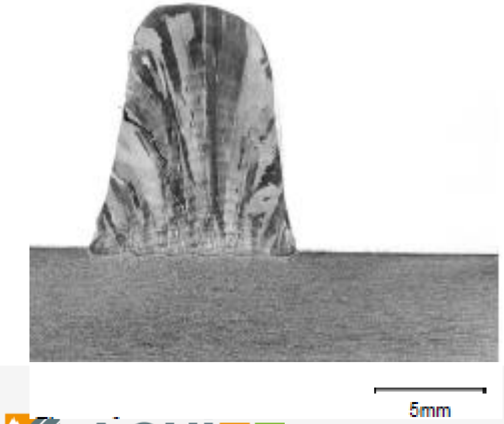
Laser Based Directed Energy Deposition (DED-LB)- SoA HESA





- ✓ Tracks and overlaps do not give any apparent problems
- ➢ Some material is ejected during manufacturing promoting severe fissures as grow in Z direction
- ➢ Analysis of ejected particles show large quantities of O and C (as DTA predicted)
- ➢ Improving argon protection, the quality is greatly enhanced although there were still cracks
- ➢ Manufacturability is an important criteria not considered in AI. Oxidation problem nor detected by CALPHAD

SoA-HESA has been used for cladding
AI HESA will be scale up for 3D printing

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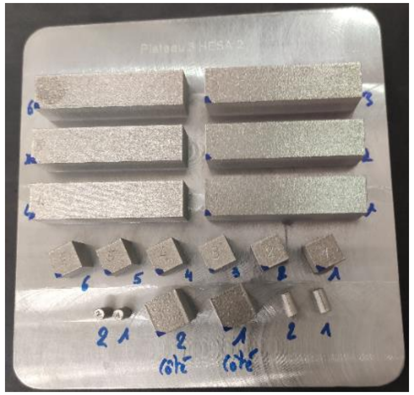
WP4: Processes

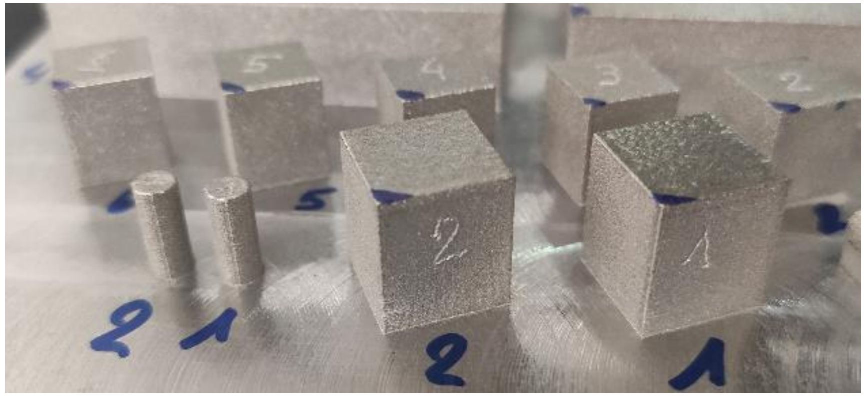
Laser Based Powder Bed Fusion (LPBF)- Al-MEA

MAIN RESULTS:

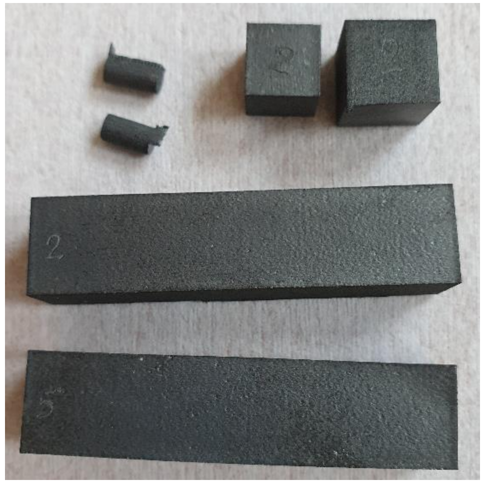
- LPBF conditions allow to obtain parts with **99.74-100 %** relative density
- **No cracks** have been detected in Al-MEA

As built LPBF samples





- 2 different TTs have been selected and applied.
- One will be used in SEM (H+A)
- Only aging for tensile, SEM, XRD and tomography



Direct aging of LPBF samples

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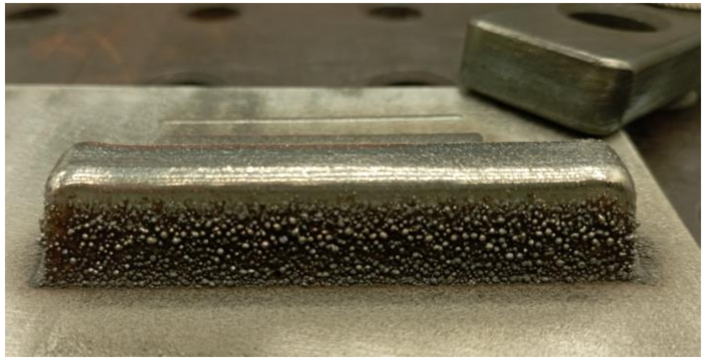
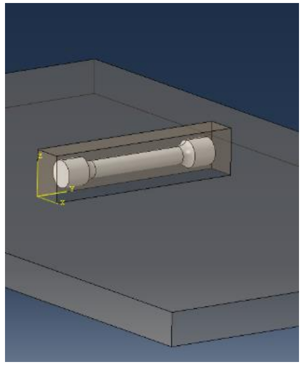
WP4: Processes

Laser Based Directed Energy Deposition (DED-LB)- Al-MEA

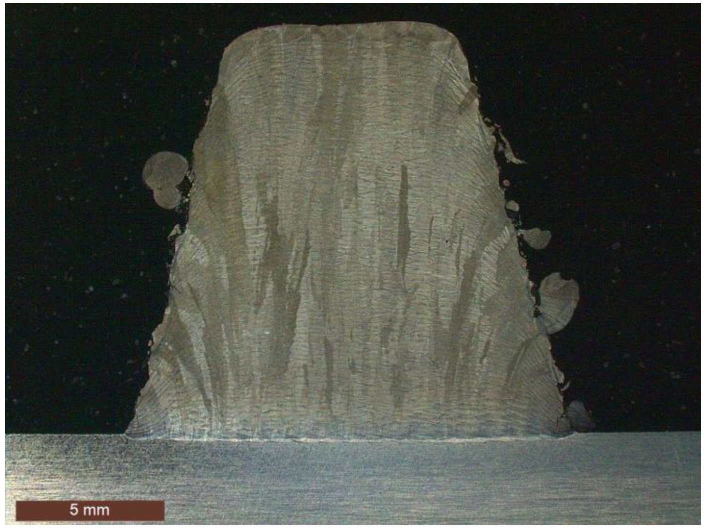
DED-LB

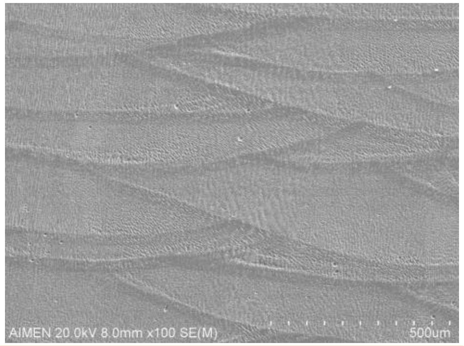


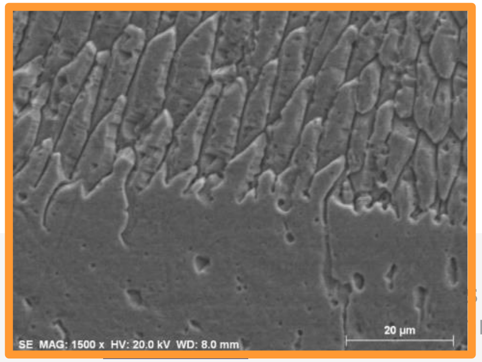


- ➢ Good manufacturability without remarkable defects. Less power needed than in SoA-HESA
- ➢ Good compromise between strength & ductility (as built condition)

Rp0,2 (Mpa)	Rm (Mpa)	A (%)	Z (%)
735	918	17	27







- ➢ Solidification microstructure with recrystallized zones
- ➢ No detectable micro-segregation of elements

IN PROGRESS
- Microstructural analysis in as-built condition, including fracture.
- FEM simulation
- Thermal treatment definition & application
- Tensile at@800ºC (as built VS TTed)
- Planned creep tests (1yr-ahead)

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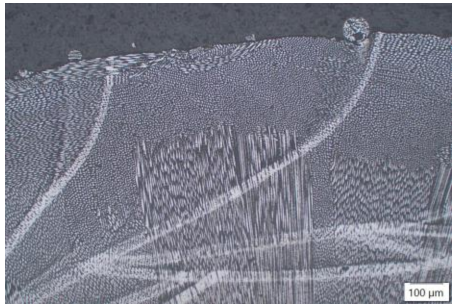
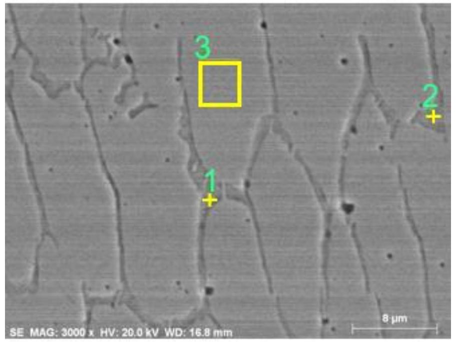
Laser Based Directed Energy Deposition (DED-LB)- Al-MEA

Heat Treatment

As-built

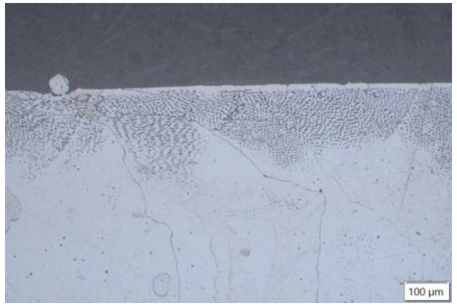


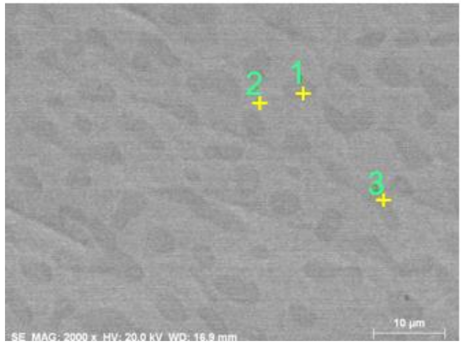


Mass percent (%)

Spectrum	C	Al	Ti	Cr	Fe	Co	Ni	Mo	W
1	2.28	9.33	0.00	0.05	24.98	29.90	33.46	0.00	0.00
2	3.19	9.82	0.00	0.00	25.26	29.58	32.14	0.00	0.00
3	3.09	5.47	0.04	0.07	29.78	32.97	28.59	0.00	0.00

TT1

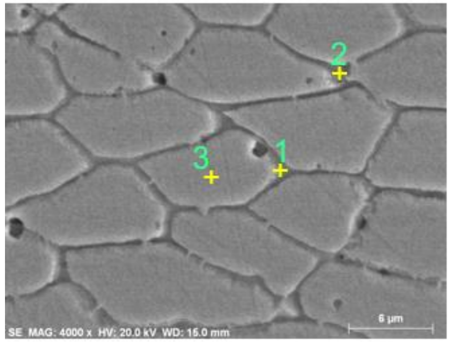




Mass percent (%)

Spectrum	C	Al	Ti	Cr	Fe	Co	Ni	Mo
1	2.49	10.62	0.00	0.19	24.01	27.90	34.80	0.00
2	2.71	12.06	0.12	0.05	20.97	27.84	36.18	0.07
3	2.92	8.61	0.03	0.00	28.33	31.05	29.06	0.00
4	3.31	5.09	0.04	0.06	30.34	32.82	28.23	0.11

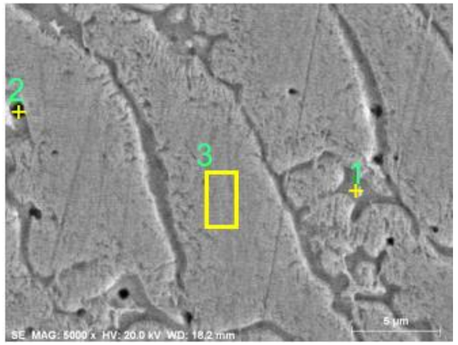
TT2



Mass percent (%)

Spectrum	C	Al	Ti	Cr	Fe	Co	Ni	Mo	W
1	1.42	7.10	0.26	0.02	29.29	30.25	31.67	0.00	0.00
2	2.21	7.33	0.06	0.21	27.35	31.66	31.18	0.00	0.00
3	1.96	5.49	0.12	0.00	29.58	33.09	29.76	0.00	0.00

TT3



Mass percent (%)

Spectrum	C	Al	Ti	Cr	Fe	Co	Ni	Mo	W
1	2.05	8.88	0.00	0.22	25.89	29.03	33.93	0.01	0.00
2	3.13	7.48	0.00	0.33	27.51	31.64	29.91	0.00	0.00
3	2.27	3.99	0.00	0.17	30.94	34.21	27.69	0.00	0.72

- Microstructure changes greatly as a function of the temperature and time
- Deep analysis is being carried out

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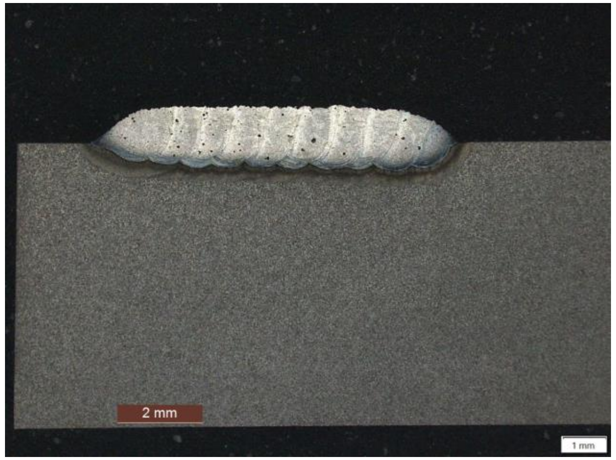
WP4: Processes

Laser Cladding- SoA-HESA

- Reinforcement: **n-TiC (4, 8.5 & 15% vol.) and m-TiC (60% vol.)**
- Laser power: 500-1100
- Speed: 5-30mm/s
- Powder Flow: 2-8g/min for nano / up to 25g/min with micro
- Gas Flow: 27L/min
- Clads: 1 & 2 layers
- Overlap: 55% and 75%



- Nano-reinforcement promotes higher dilution
- Better hardness achieved is around 450Hv

- Micro-reinforcement promotes lower dilution
- Better hardness achieved is > 850Hv
- Large dispersion due to the size of the reinforcement

The project has received funding from the European Union's Horizon 2020 research and innovation program under Grant Agreement N° 958374.

OUTLOOK/NEXT STEPS IN WP4

DED & PBF

- Deeper microstructural analysis in as-built condition, and comparison after thermal treatment.
- Thermal treatment application to testing specimens
- Tensile at@800ºC (as built VS TTed)
- TT- creep tests
- To scale up atomized Al-MEA up to 150kg (for WP7)

LC

- Process parameters optimization
- HT wear tests for HEAs MMCs coatings

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Thank you

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