Differential Thermal Analysis to Assist the Design of Corrosion-resistant High Entropy Alloys for Laser Powder Bed Fusion

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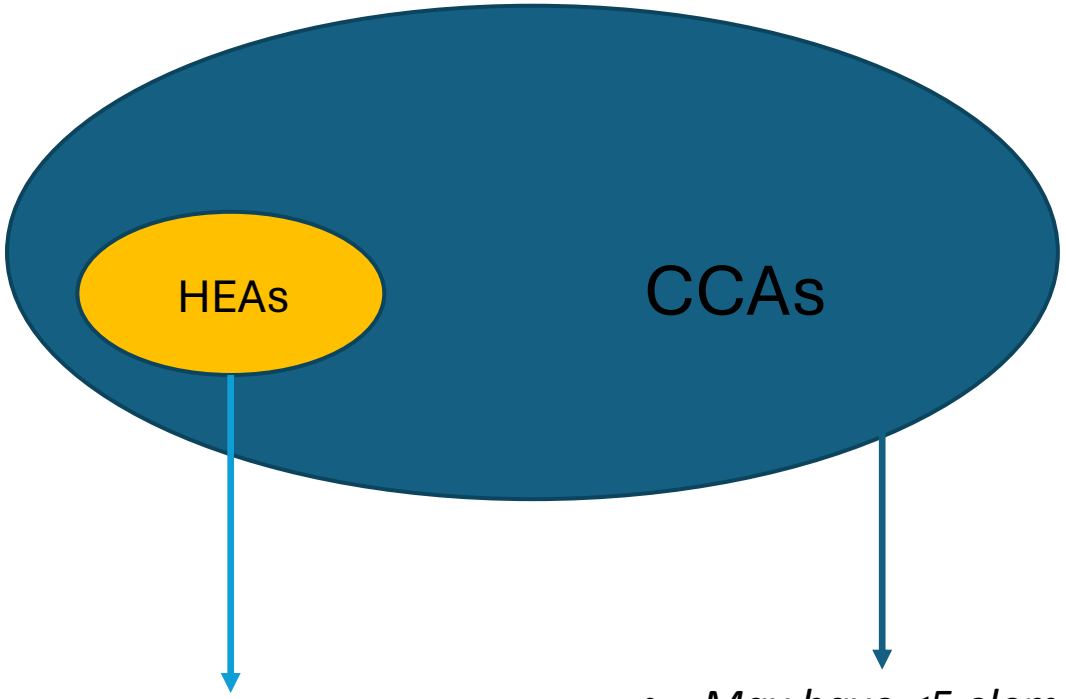
Introduction



- *5+ elements*
- *Single-phase solid solution*
- *High configurational entropy*

- *May have <5 elements*
- *>35% of elements*
- *Multiple phases, Intermetallics (IM) included*
- *Entropy does not matter*

The common phases are FCC and BCC, while the IM are B2, Sigma and Laves.

BCC

- High Hardness
- Good electrical and thermal conductivity
- Low thermal expansion
- Good ductility

FCC

- Greater mechanical strength
- Better wear resistance
- Better corrosion resistance
- Better ductility

The goal of this study is to design a corrosion-resistant HEA through LPBF

Crystal Structure Prediction

$\Omega = Tm\Delta S_{mix} / \Delta H_{mix}$ $\quad \Omega \geq 1.1$

δ: atomic size difference $\quad \delta \leq 6.6\%$

VEC: Valence electron concentration

Stable, Solid-solution phase

$$\mathrm{VEC} = \sum_{k=1}^{n} (c_i) VEC_i$$

$VEC \geq 8$  FCC

$6.87 \leq VEC < 8$  FCC + BCC

$VEC < 6.87$  BCC

TABLE I. Physiochemical properties for commonly used elements in HEAs.

Element	Atom radius (Å)	Pauling electronegativity	VEC
Al	1.432	1.61	3
B	0.820	2.04	3
C	0.773	2.55	4
Co	1.251	1.88	9
Cr	1.249	1.66	6
Fe	1.241	1.83	8
Mn	1.350	1.55	7
Mo	1.363	2.16	6
Nb	1.429	1.6	5
Ni	1.246	1.91	10
Ta	1.430	1.50	5
Ti	1.462	1.54	4
V	1.316	1.63	5
W	1.367	2.36	6

Guo S. et al., *J. Appl. Phys.* 15 May 2011; 109 (10): 103505. https://doi.org/10.1063/1.3587228

Materials and Methods

Differential Thermal Analysis (DTA)

↓

Pre-screening of compositions

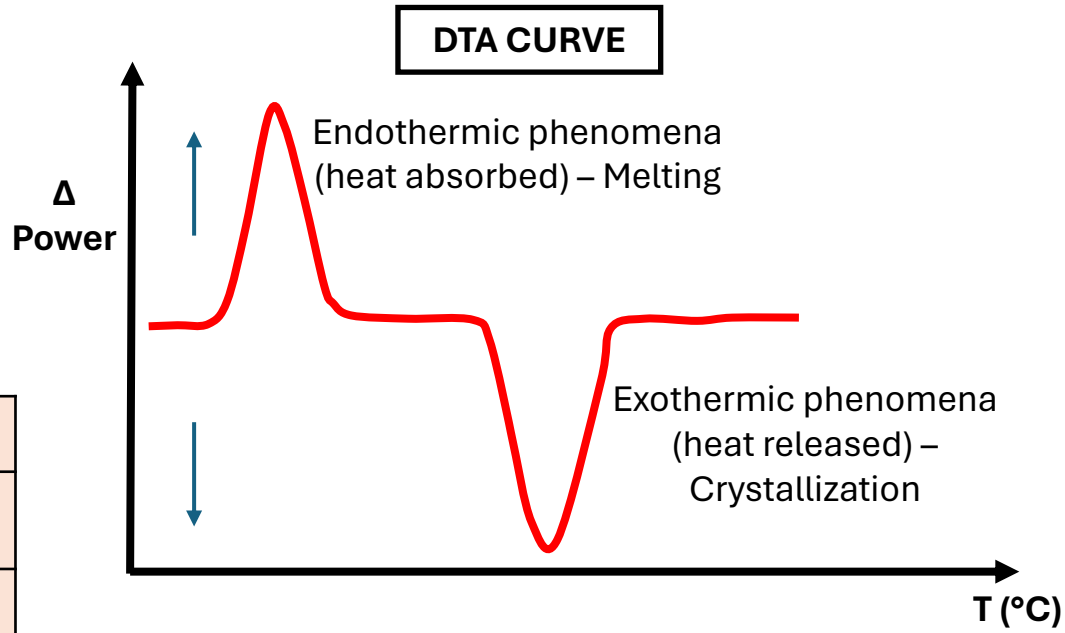
Selected elements: Al, Cr, Fe, Mn, and Ni

CrFeMnNi-based MEA

% at.	Cr	Fe	Mn	Ni	VEC
CrFeMnNi	25	25	25	25	7.75
Cr_2Fe_2MnNi	33.33	33.33	16.67	16.67	7.50
$CrFe_2MnNi_2$	16.67	33.33	16.67	33.33	8.17

AlCrFeMnNi-based HEA

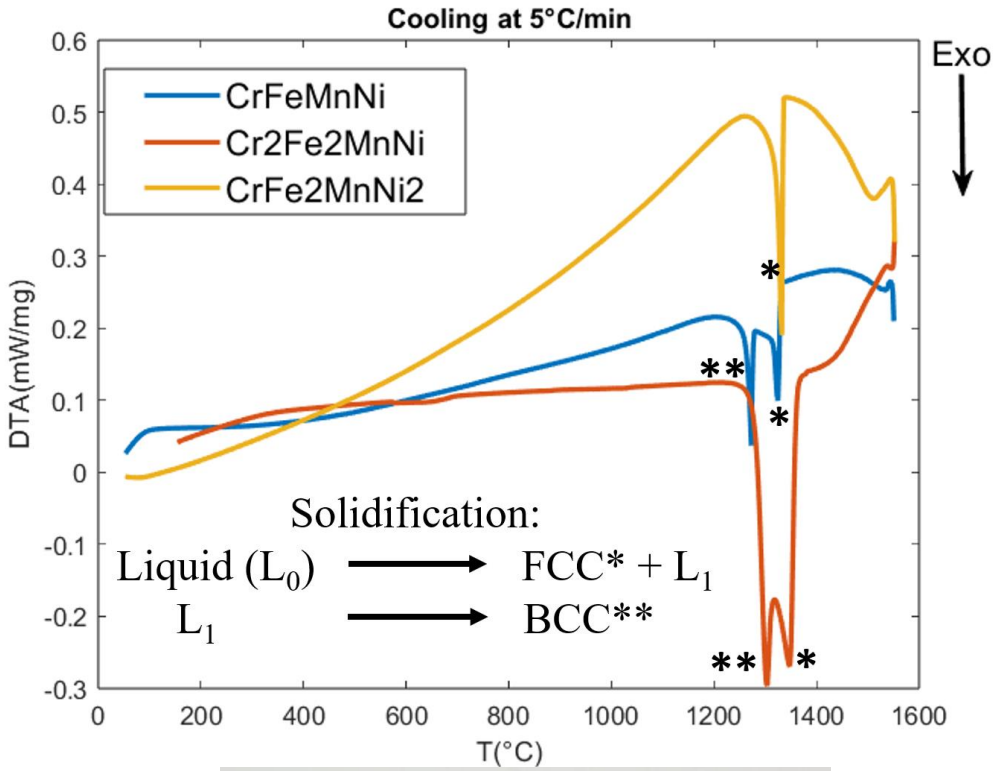
% at.	Al	Cr	Fe	Mn	Ni	VEC
AlCrFeMnNi	20	20	20	20	20	6.80
$AlCrFe_2MnNi_2$	14.29	14.29	28.57	14.29	28.57	7.43
$AlCrFe_2Ni_2$	16.67	16.67	33.33	-	33.33	7.50

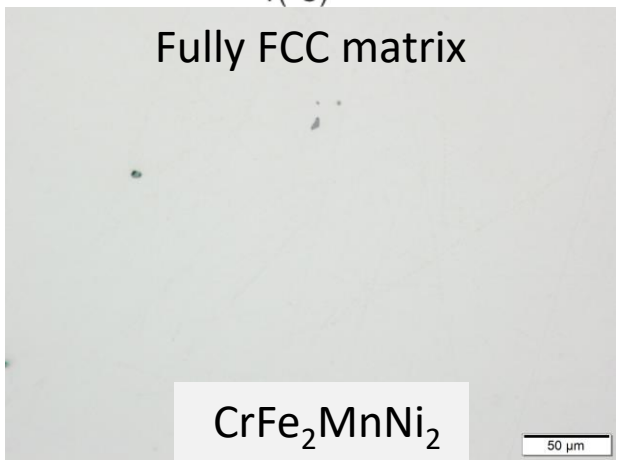


Heating up to 1550 °C at 5 °C/min

CrFeMnNi-based MEA: Solidification sequence

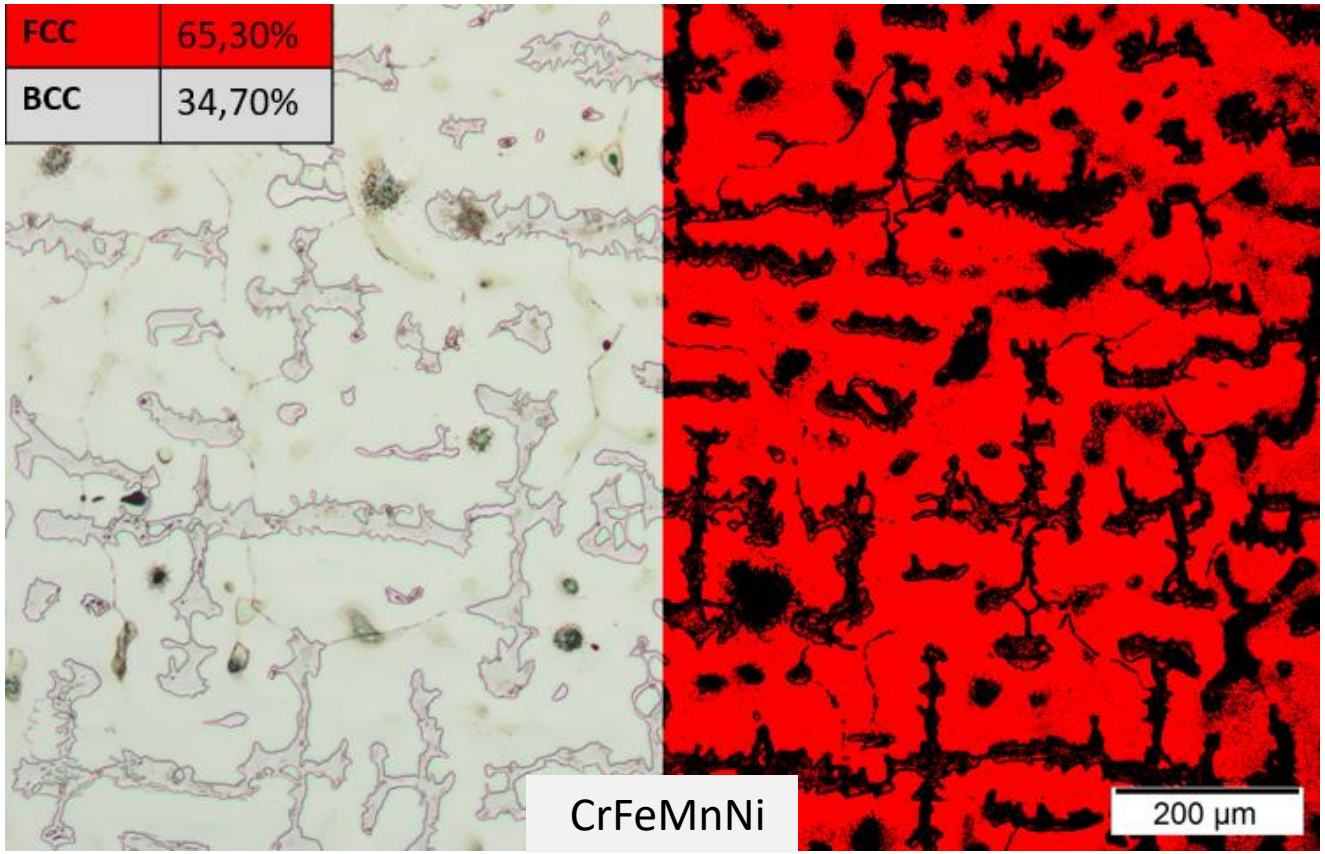
% at.	Cr	Fe	Mn	Ni	VEC
CrFeMnNi	25	25	25	25	7.75
Cr_2Fe_2MnNi	33.33	33.33	16.67	16.67	7.50
$CrFe_2MnNi_2$	16.67	33.33	16.67	33.33	8.17



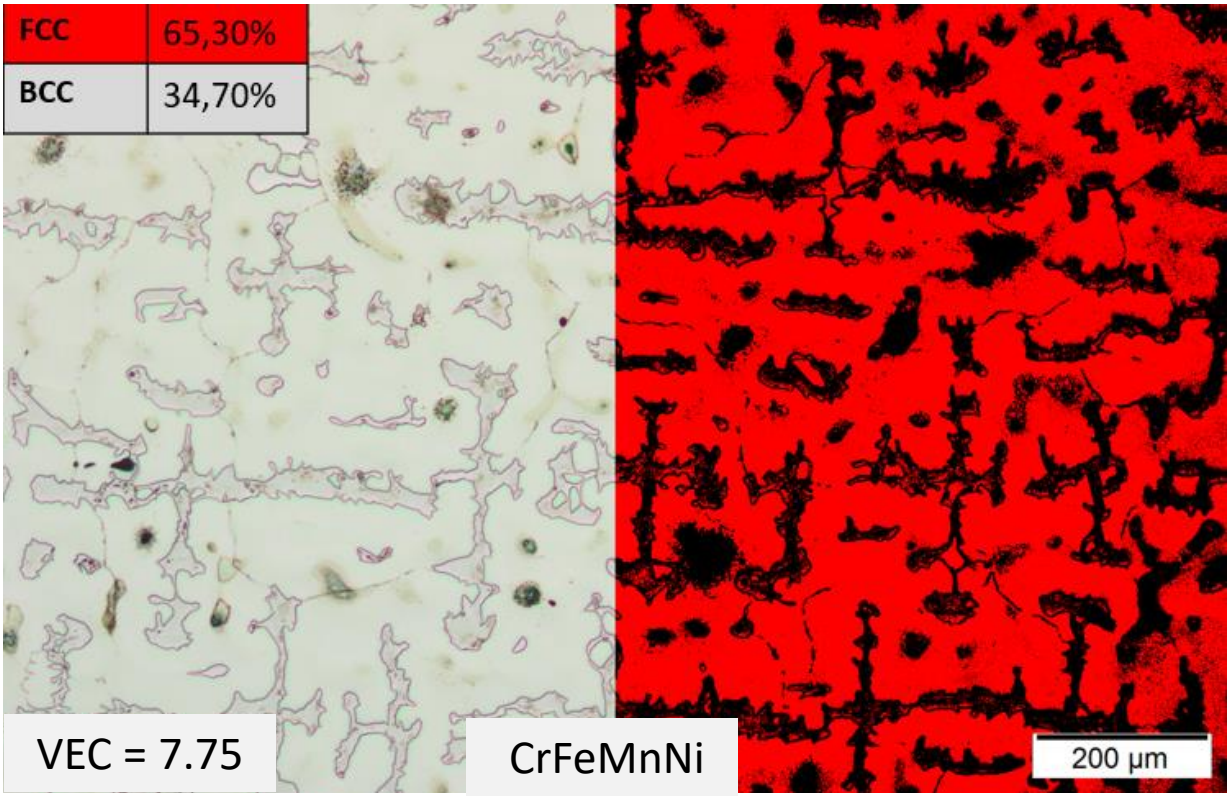


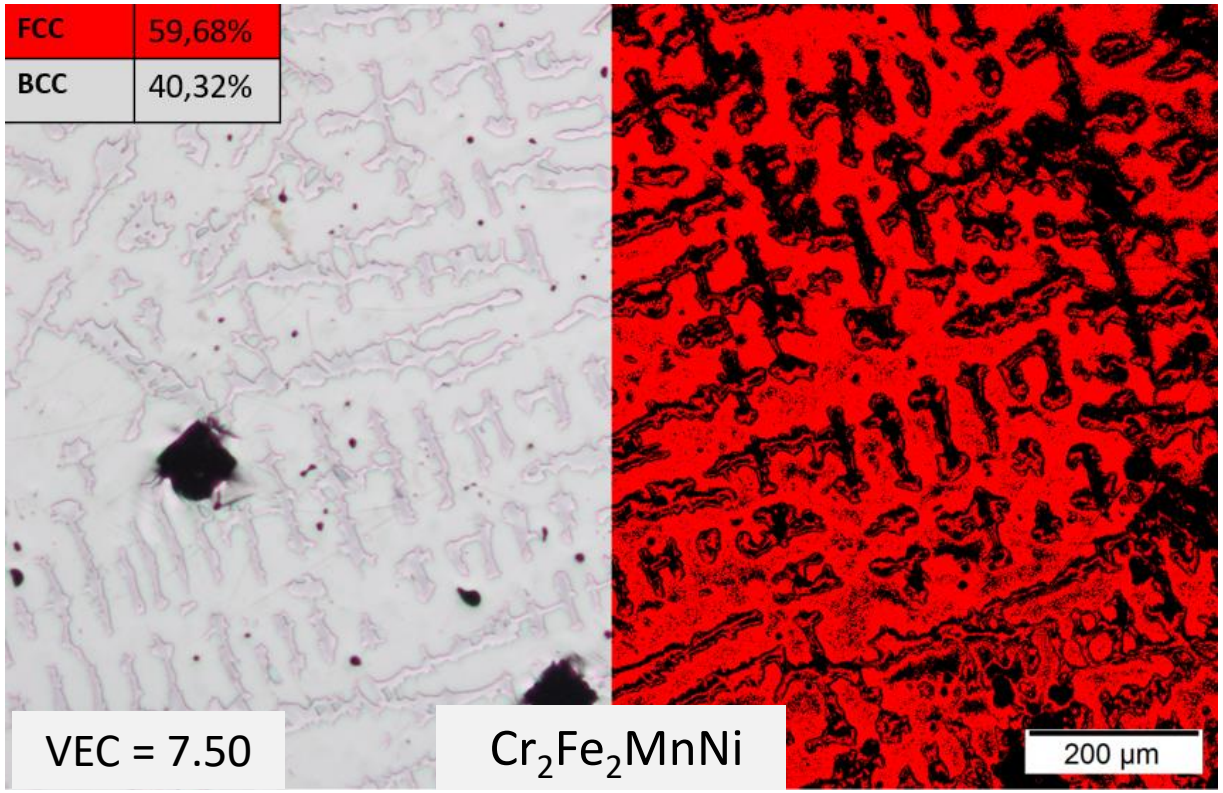
$$6.87 \leq VEC < 8$$

BCC FCC



CrFeMnNi-based MEA: Composition and quantification of the phases

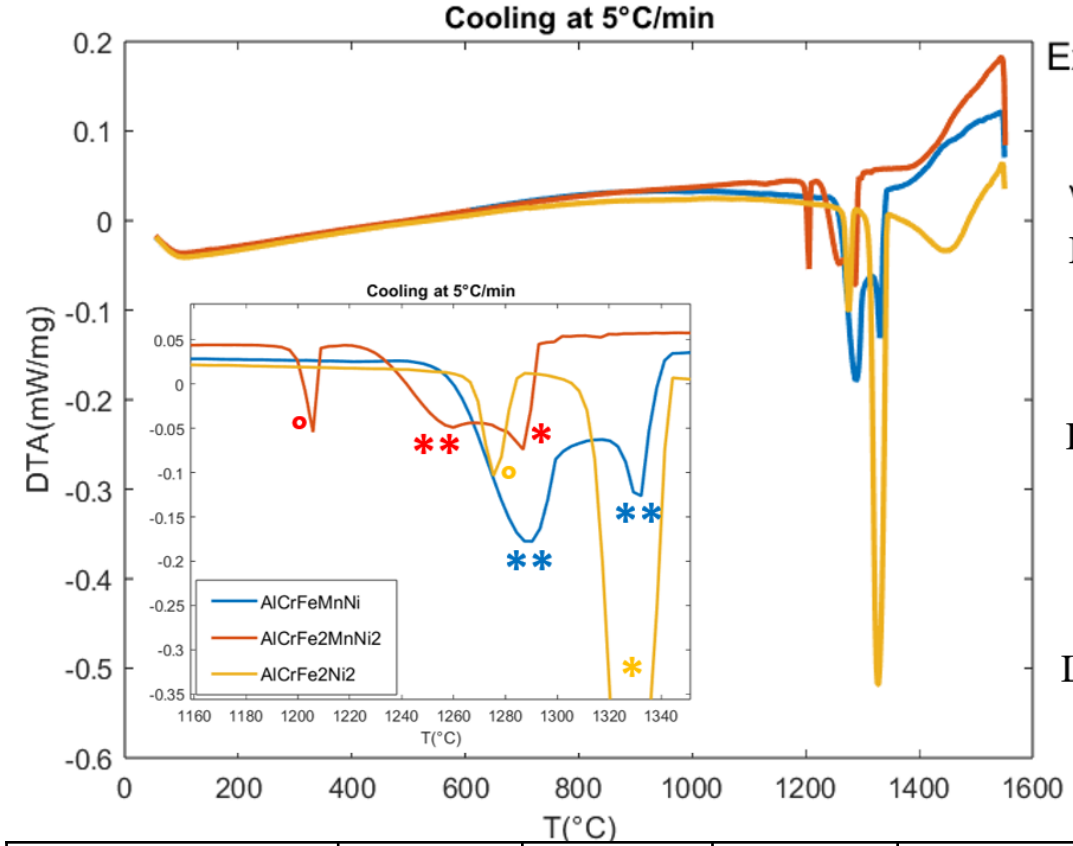




% at.	Cr	Fe	Mn	Ni
BCC	**46.2 ± 2.0**	30.3 ± 1.0	17.5 ±0.4	6.0 ± 1.4
FCC	25.0 ± 1.4	29.5 ± 2.5	26.0 ± 2.0	**19.5 ± 1.7**

% at.	Cr	Fe	Mn	Ni
BCC	**47.0 ± 0.7**	33.2 ± 0.5	10.9 ± 0.4	8.9 ± 0.5
FCC	28.4 ± 1.0	34.8 ± 1.5	14.8 ± 1.0	**22.0 ± 1.4**

AlCrFeMnNi-based HEA: Solidification sequence



$AlCrFeMnNi$

$\text{Liquid } (L_0) \rightarrow BCC^{**} + L_1$

$L_1 \rightarrow BCC^{**}$

$AlCrFe_2MnNi_2$

$\text{Liquid } (L_0) \rightarrow FCC^{*} + L_1$

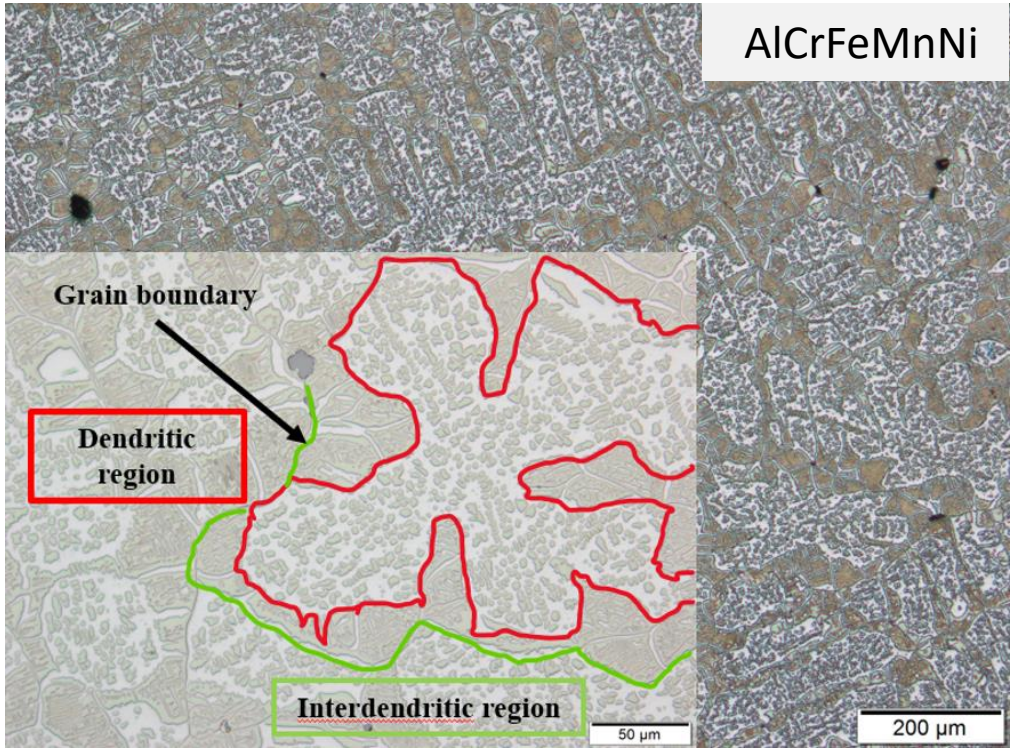
$L_1 \rightarrow BCC^{**} + L_2$

$L_2 \rightarrow FCC/BCC^{\circ}$

$AlCrFe_2Ni_2$

$\text{Liquid } (L_0) \rightarrow FCC^{*} + L_1$

$L_1 \rightarrow FCC/BCC^{\circ}$



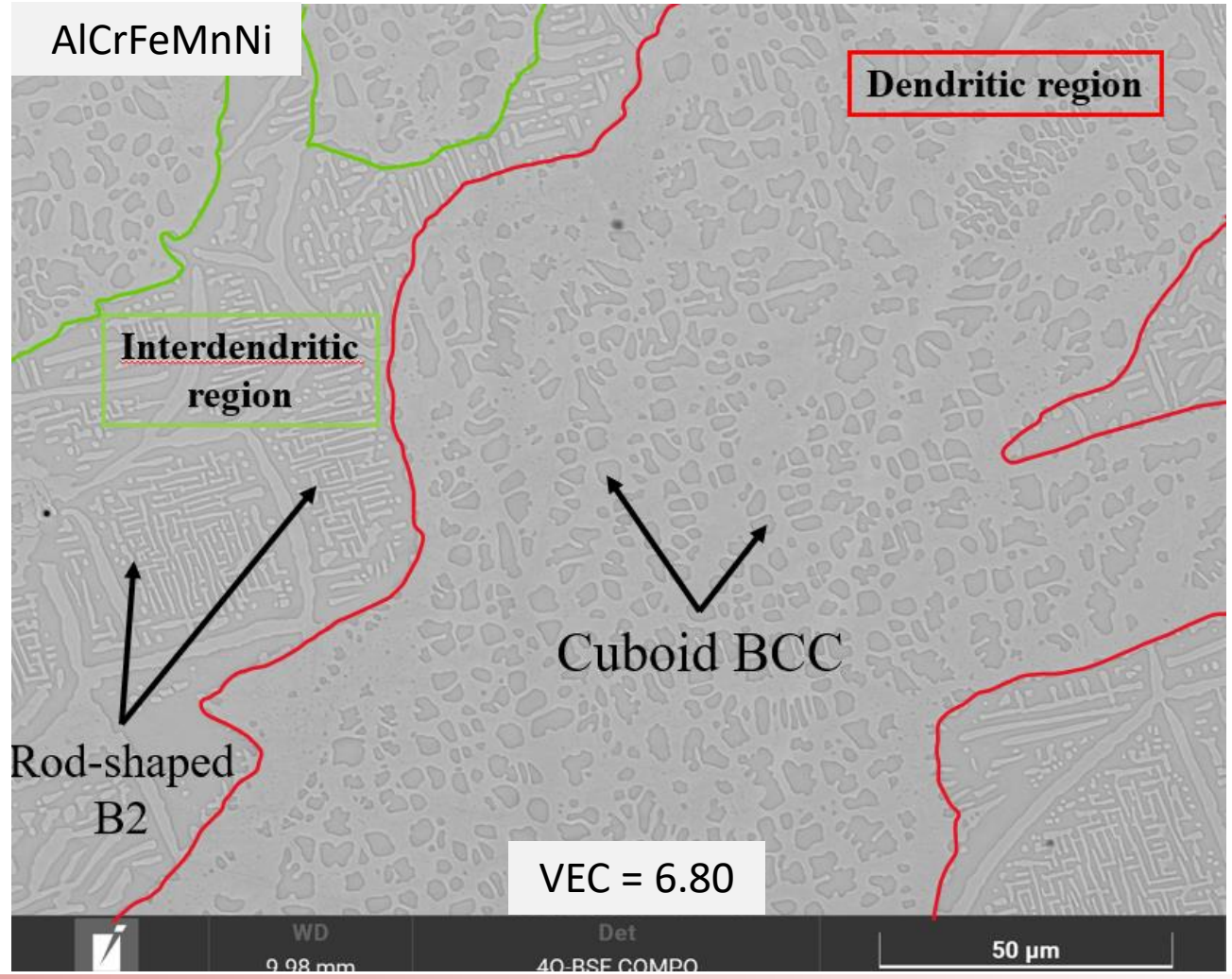
% at.	Al	Cr	Fe	Mn	Ni	VEC
AlCrFeMnNi	20	20	20	20	20	6.80
$AlCrFe_2MnNi_2$	14.29	14.29	28.57	14.29	28.57	7.43
$AlCrFe_2Ni_2$	16.67	16.67	33.33	-	33.33	7.50

$$6.87 \leq VEC < 8$$

BCC FCC

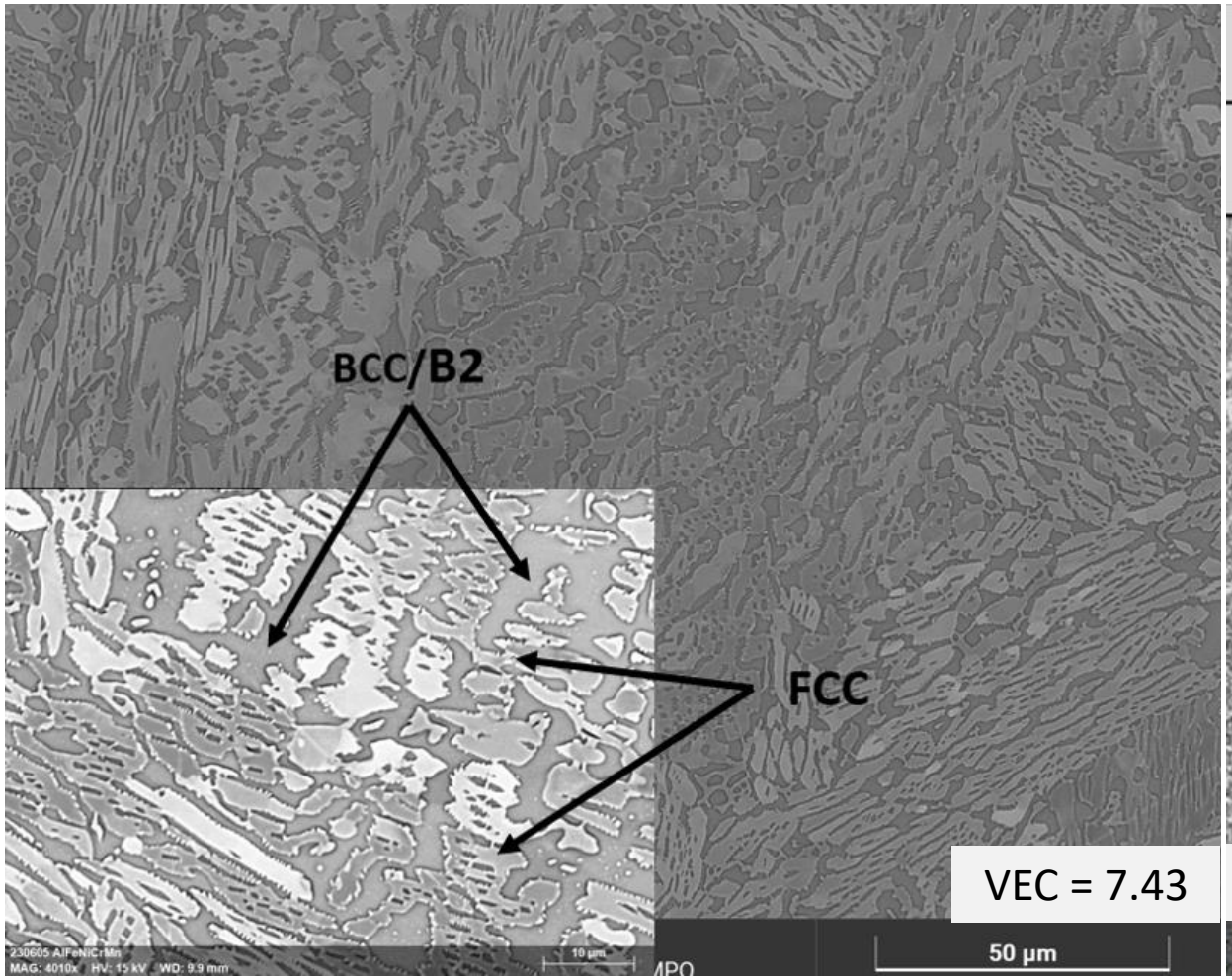
AlCrFeMnNi-based HEA:
Composition of the phases

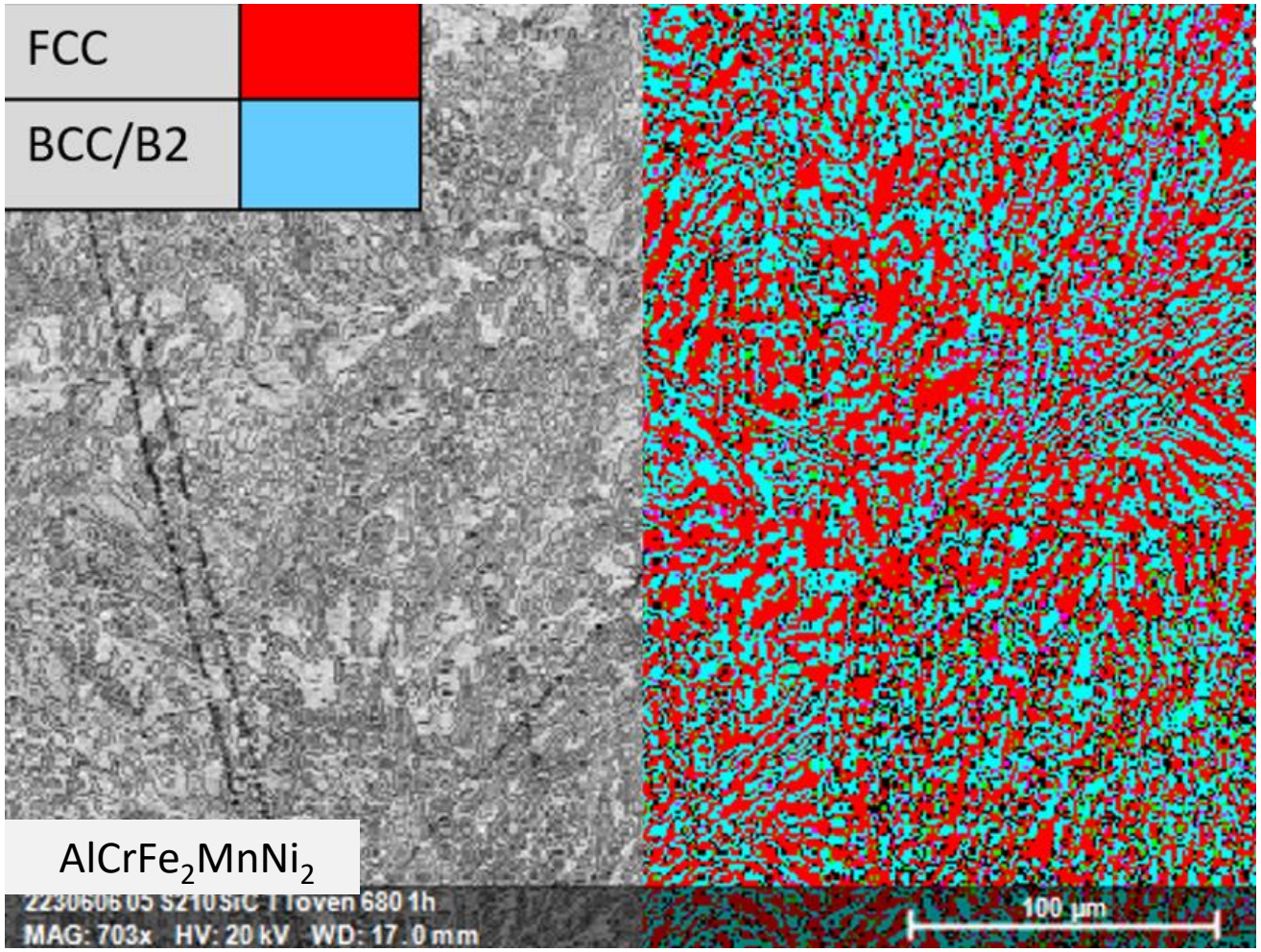
% at.	Al	Cr	Fe	Mn	Ni
Precipitates	**29.4 ± 4.0**	6.5 ± 3.0	9.0 ± 4.3	16.0 ± 1.5	**39.1±7.9**
Matrix	7.7 ± 1.1	**34.6 ± 1.8**	**30.0 ± 0.9**	24.7 ± 0.5	3.1 ± 1.6



AlCrFeMnNi-based HEA:
Composition and EBSD analyses

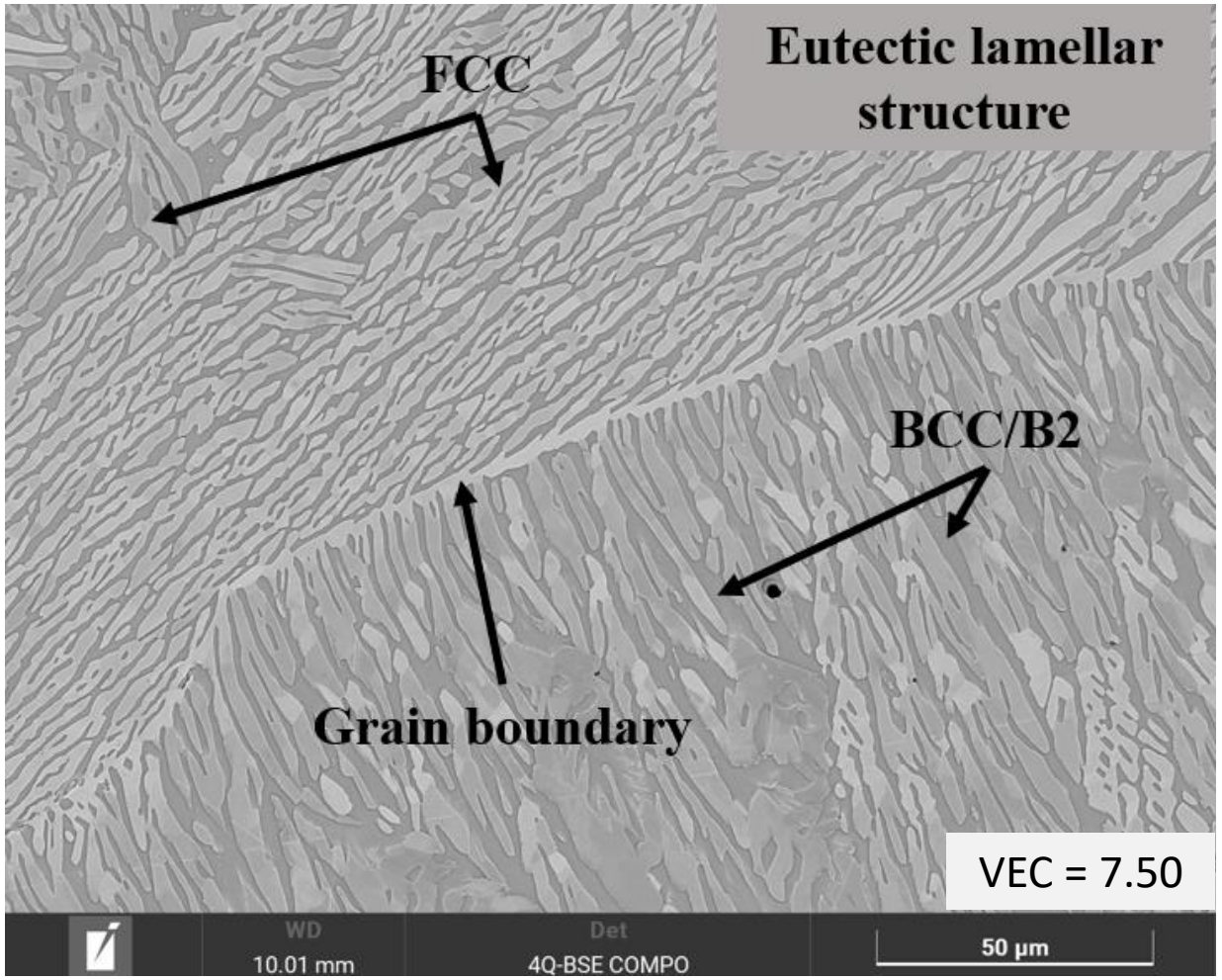
% at.	Al	Cr	Fe	Mn	Ni
FCC	4.7 ± 0.4	**18.6 ± 0.9**	**39.6 ± 0.6**	14.2 ± 0.3	22.9 ± 0.8
B2	**26.0 ± 0.6**	2.1 ± 0.2	7.9 ± 0.4	15.9 ± 0.5	**48.1 ± 0.5**
BCC	**20.7 ± 4.3**	9,3 ± 6.8	14.3 ± 1.4	15.4 ± 7	**38.4 ± 9.8**

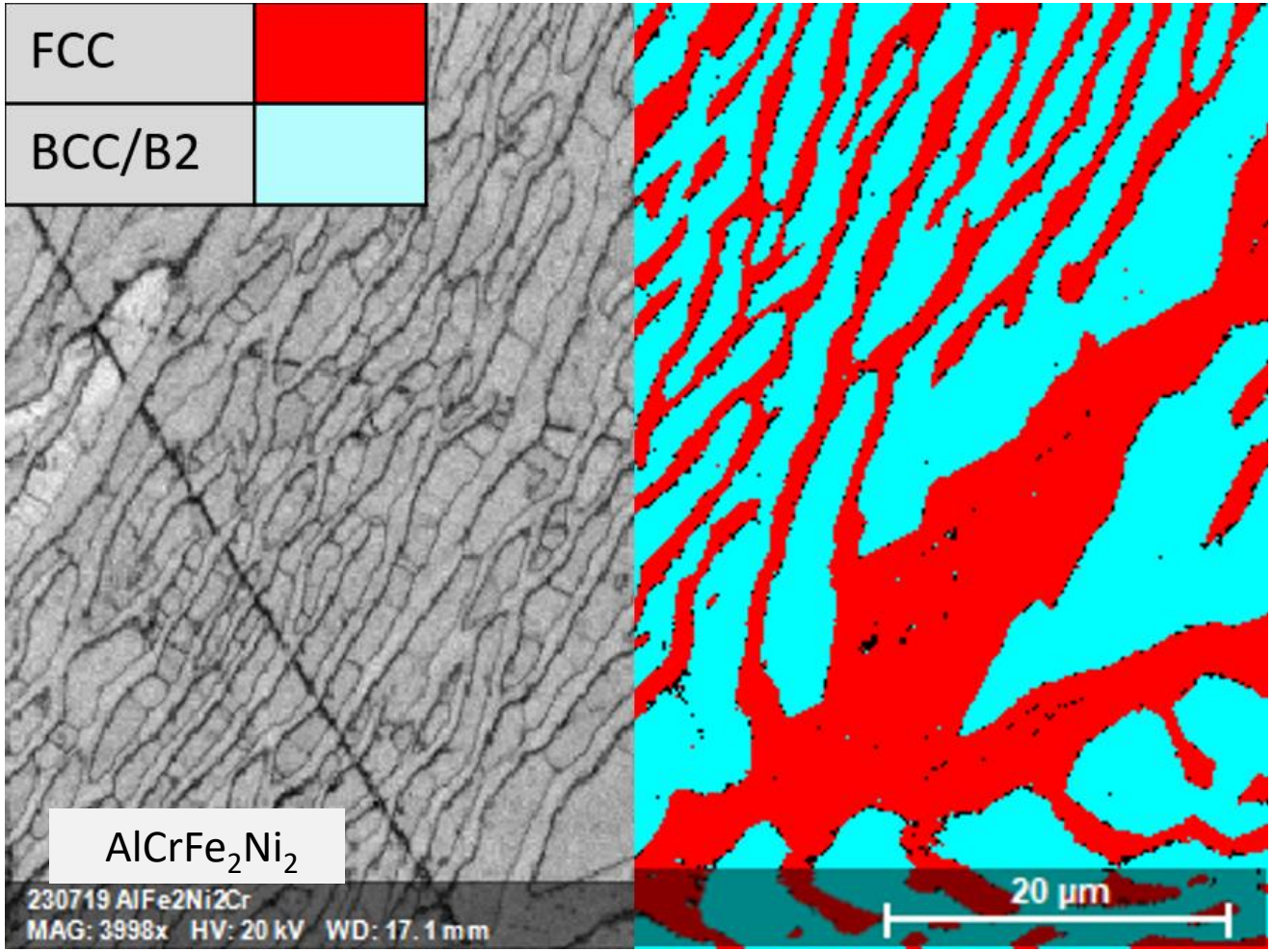




AlCrFeMnNi-based HEA:
Composition and EBSD analyses

% at.	Al	Cr	Fe	Ni
FCC	6.8 ± 0.5	**22.8 ± 0.1**	**41.9 ± 1.1**	28.4 ± 0.7
B2	**29.7 ± 1.2**	4.9 ± 0.4	14.2 ± 0.6	**51.1 ± 0.2**
BCC	**27.0 ± 1.5**	10.41 ± 2.9	18.6 ± 1.8	**44.0 ± 3.1**





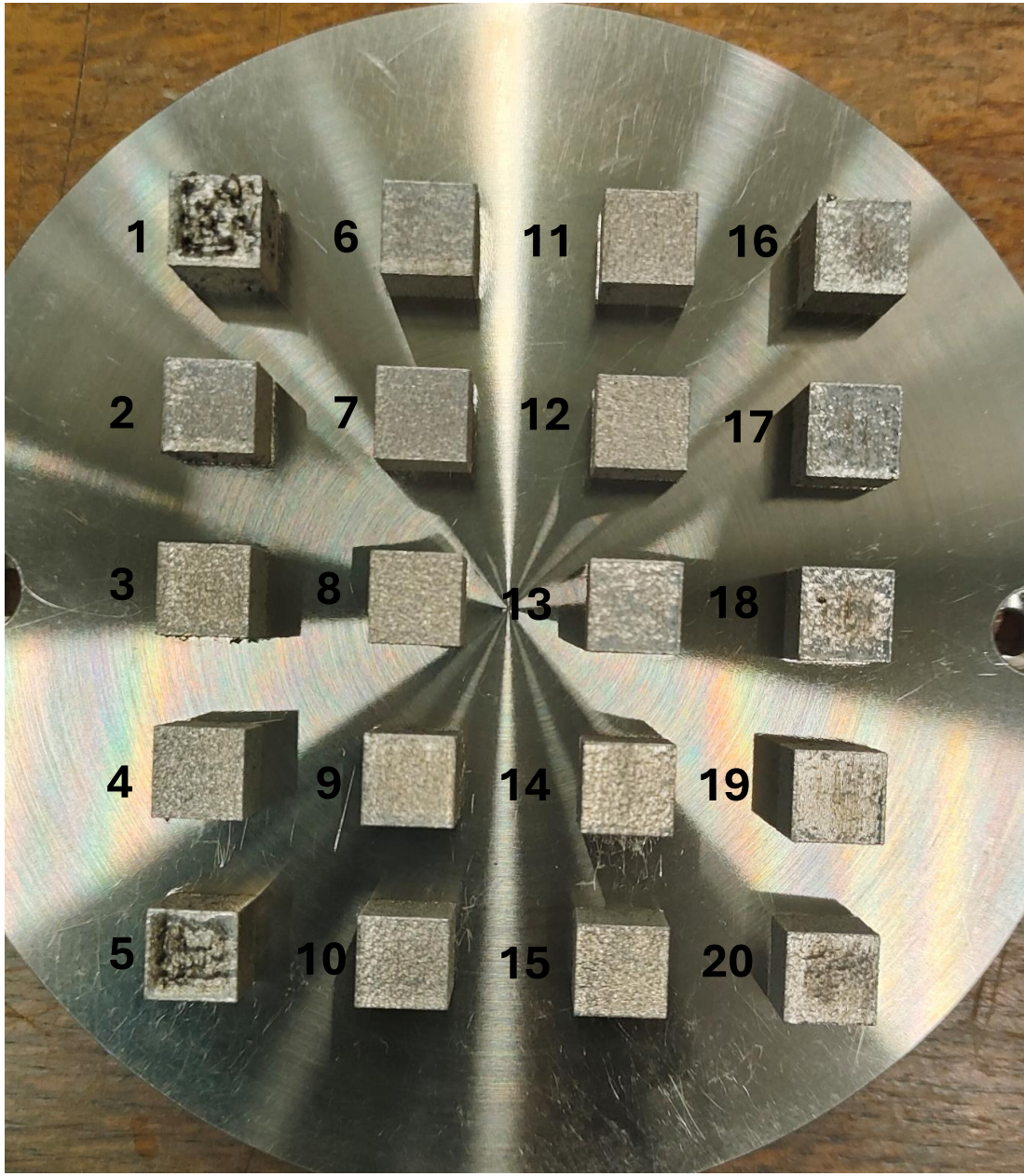
Conclusions

- VEC crystal prediction theory is a useful tool to predict the first phases that solidify
- VEC theory does not consider solid-state transformations
- In Al, Cr, Fe, Mn and Ni system, FCC phase is Cr-Fe rich while BCC phase is rich in Al and Ni
- Al promotes the BCC formation, followed by spinodal decomposition

- DTA is a rapid and cost-effective test to investigate the transformations that occur at near-equilibrium conditions
- The near-equilibrium results are used to understand the out-of-equilibrium phenomena and mechanisms of LPBF
- This method guide the design of new alloys and the thermal treatments

Perspectives

- A composition has been chosen for LPBF
- The parameters of the LPBF were optimized
- Cubic samples were printed



Surface and microstructural characterization

Thanks for your attention

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