INL/CON-23-75852-Revision-0

Design and development of equi-atomic high entropy alloys for use in irradiation environments

December 2023

Changing the World's Energy Future

Anilas Karimpilakkal, Joseph Newkirk, Jason L Schulthess, Frank Liou

Idaho National Laboratory

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MATERIALS IN NUCLEAR ENERGY SYSTEMS

Design and development of equi-atomic high entropy alloys for use in irradiation environments

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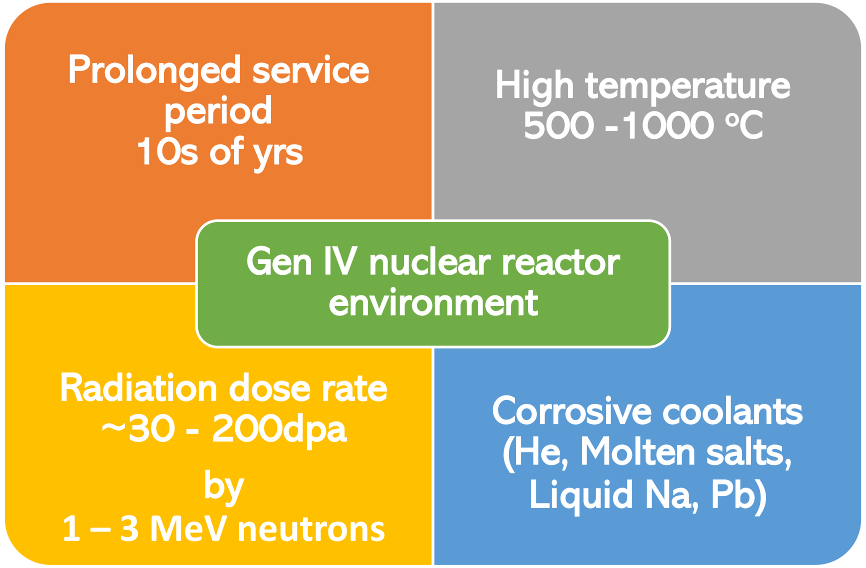
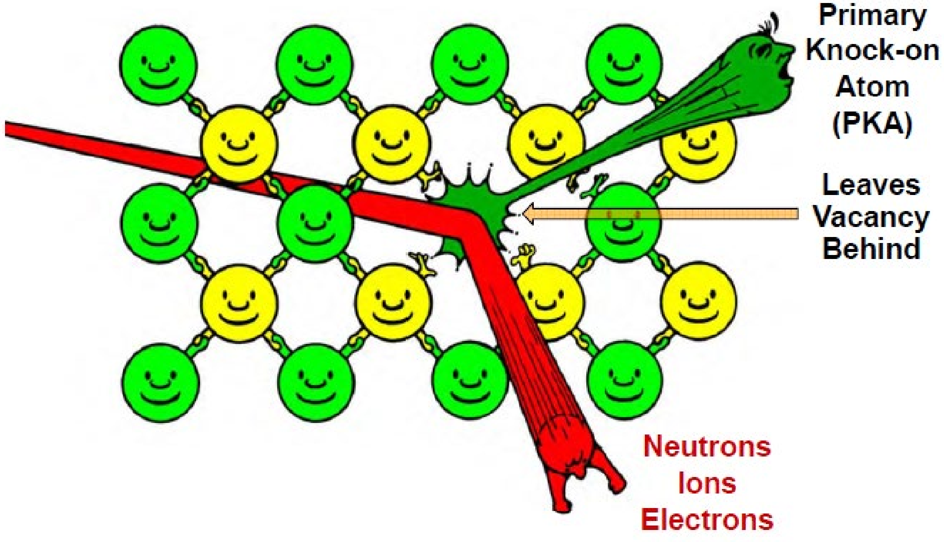
Background

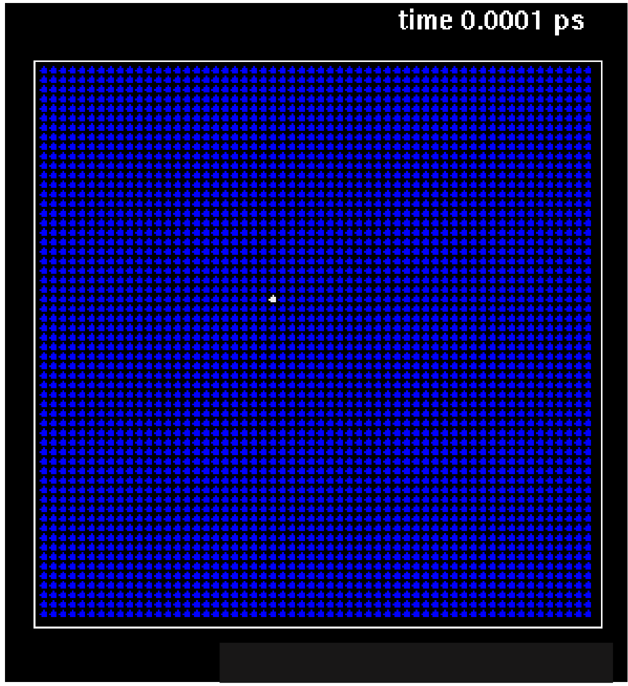
- Ever growing energy need and carbon footprint free sources → Generation (Gen) IV reactors!!
- Structural materials in nuclear environments → degradation of properties & failure !!
- New Materials with better irradiation properties → High Entropy Alloys(HEAs)[1,2].



Fukushima nuclear accident 2011

Radiation damage





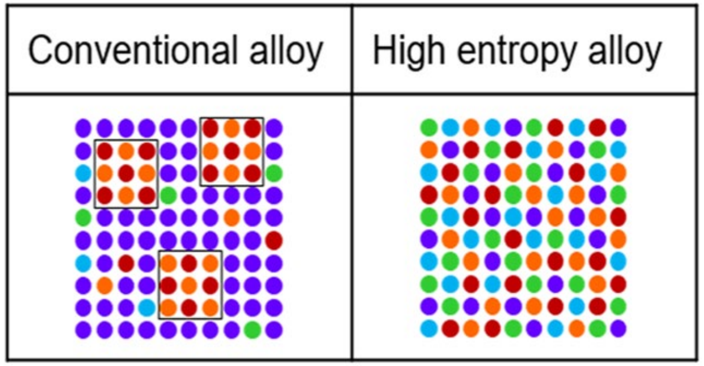
Collision cascade induced by a 10keV recoil in Au at 0K temperature [3]

- Ballistic collision → high energy particle and atoms
- Displacement cascade → Frenkel pairs, FP.
- Thermal spike → localized heating & recombination of FPs.
- Annealing → surviving FPs.
- Diffusion of FPs → extended defects.

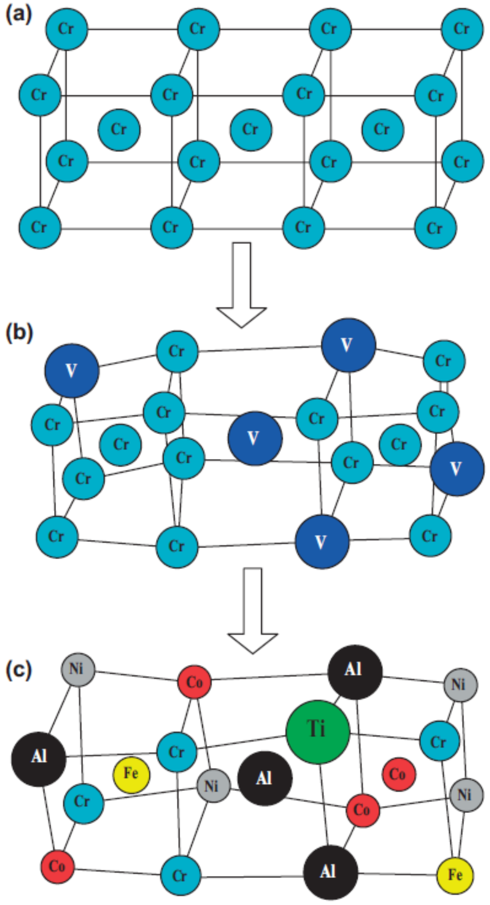
HEAs ??

- HEAs are proved to possess
  - higher resistance to defect formation [1]
  - lower void swelling [2]
  - higher microstructural stability under irradiation [2]
  - limited irradiation hardening [2]

- These are due to
  - poor thermal conductivities → promote recombination of FPs
  - sluggish diffusion → lesser extended defects
  - higher defect energetics →lower damage accumulation



[4]



Schematic illustration of BCC crystal structure : (a) Cr (b) Cr-V solid solution distorted lattice (c) seriously distorted AlCoCrFeNiTi0.5 system [Zhang]

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Selection of nuclear friendly elements

Elements and their properties

Elements	r [Å]	T_m [K]	ρ [g/cm^3]	χ	σ_A [barns]
Al	1.432	933	2.72	1.47	0.231
Ti	1.462	1941	4.51	1.32	6.09
V	1.340	2183	6.12	1.45	5.08
Cr	1.249	2180	7.19	1.56	3.05
Zr	1.600	2128	6.51	1.22	0.185
Nb	1.429	2750	8.58	1.23	1.15
Mo	1.363	2896	10.23	1.30	2.48

- Trade off b/w σ_A, T_m, r and ρ.
- Low melting Al → low σ_A and ρ.
- Hf, Ta, W → avoided for σ_A and ρ.
- Atomic size diff <15% → solid solution according to HRR

CALPHAD modelling*

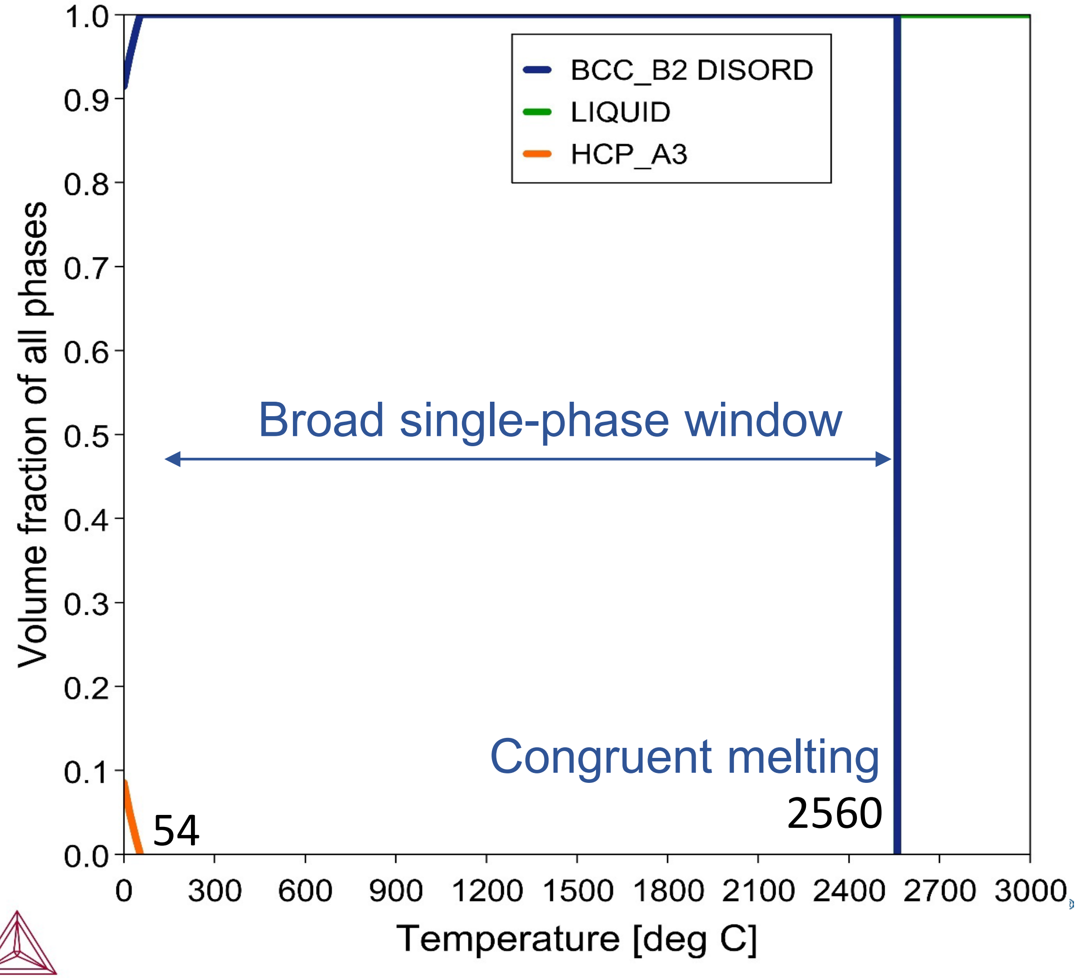
- Using Thermo-Calc2022b, TCHEA6 database
- 2 routes for Phase prediction
  - Equilibrium diagram route → assumes infinitely slow cooling
  - Non equilibrium diagram route → assumes negligible diffusion in solid state

Systems and their composition

System	Composition [at %]
D I	**MoNbTi** ← Base system
D II	MoNbTiZr
D III	MoNbTiCr
D IV	MoNbTiV
D V	MoNbTiAl
D VI	MoNbTiZrV
D VII	MoNbTiCrV
D VIII	MoNbTiCrAl
D IX	MoNbZrCrAl

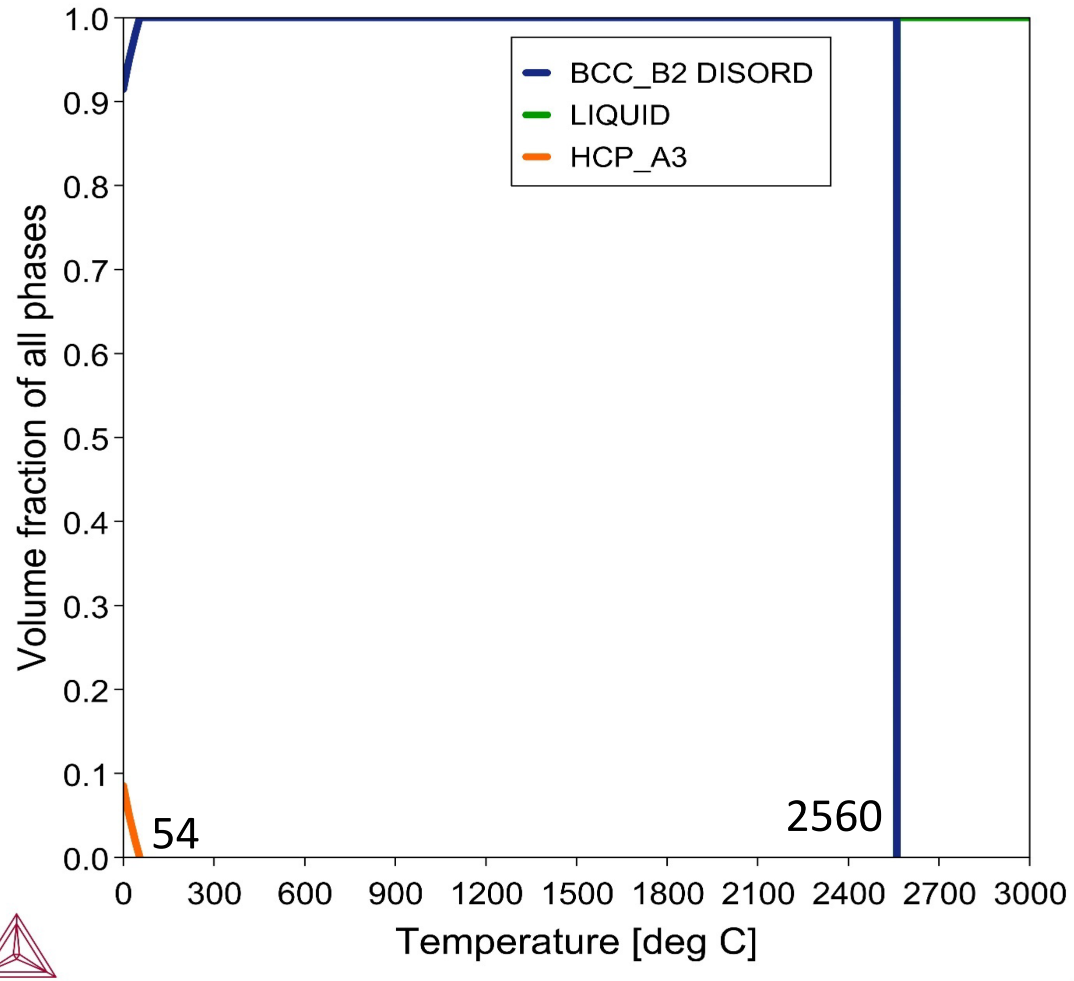
- Playing around with different combinations of elements

Mo + Nb +Ti

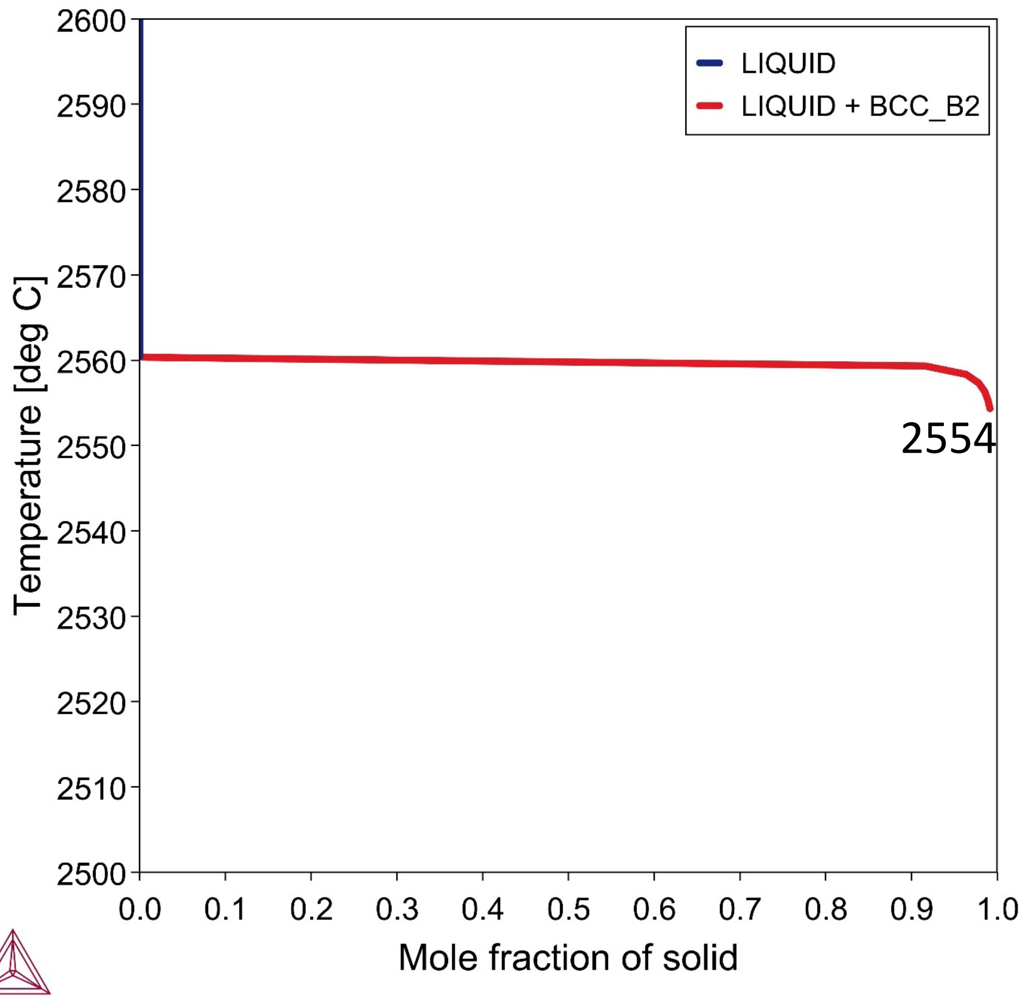


CALPHAD modelling – DI MoNbTi

(a)

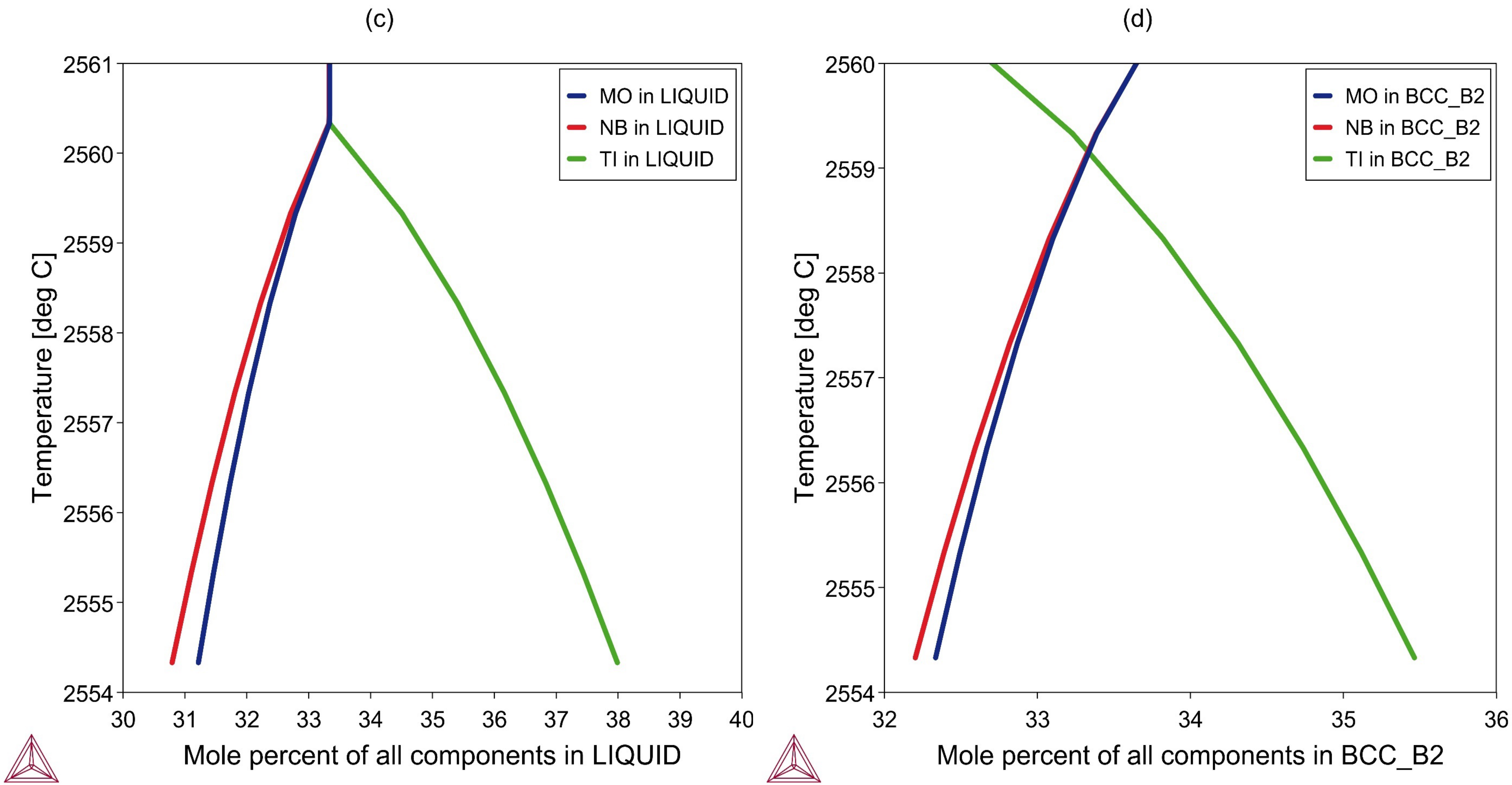


(b)



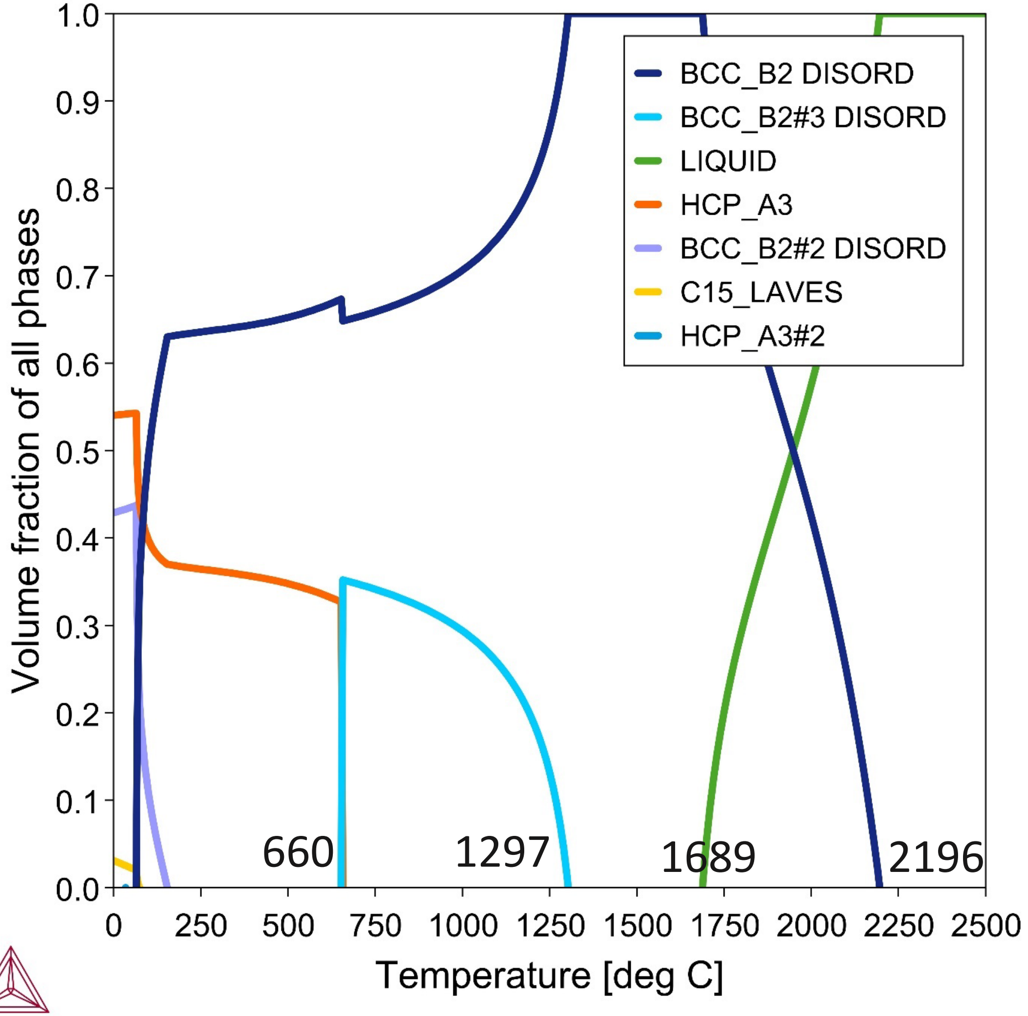
CALPHAD modelling – DI MoNbTi

- Microstructure prediction →Elemental compositional map for a phase



CALPHAD modelling – DII MoNbTiZr

(a)



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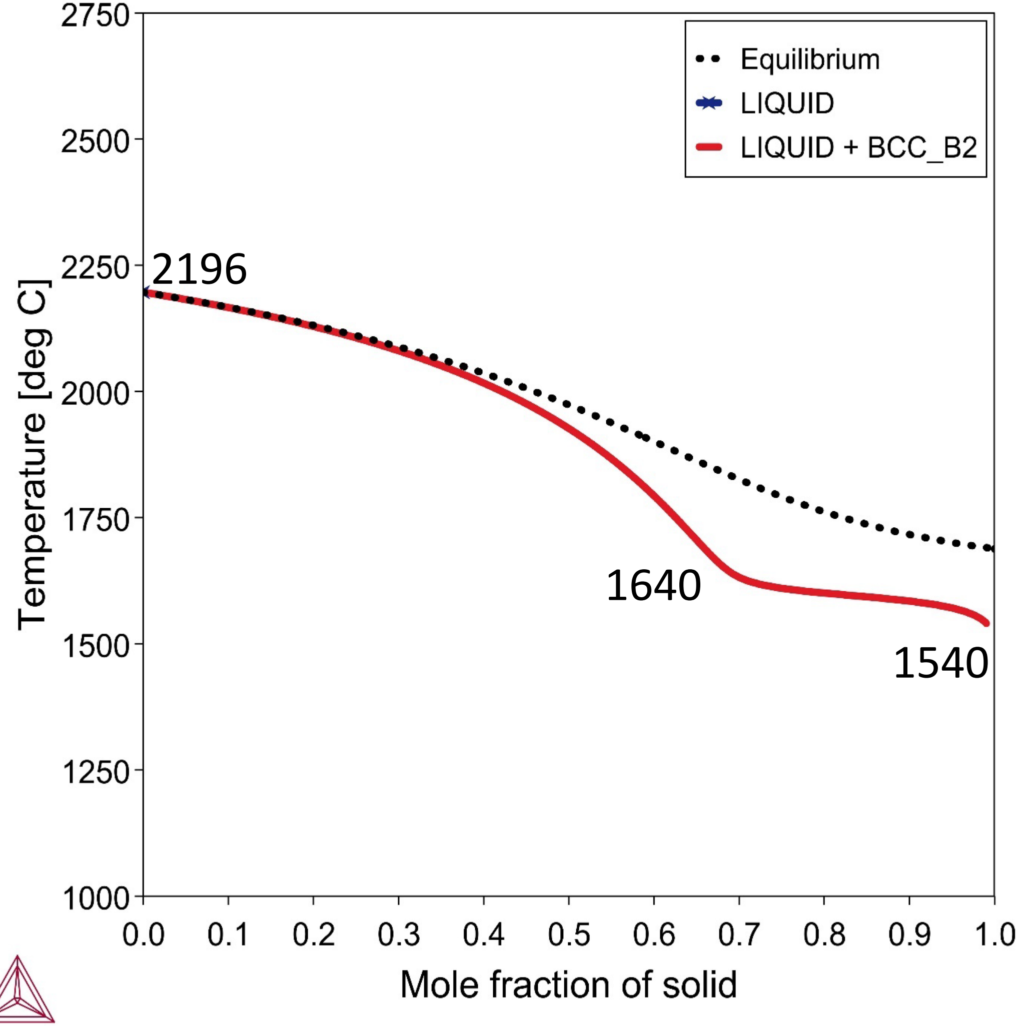
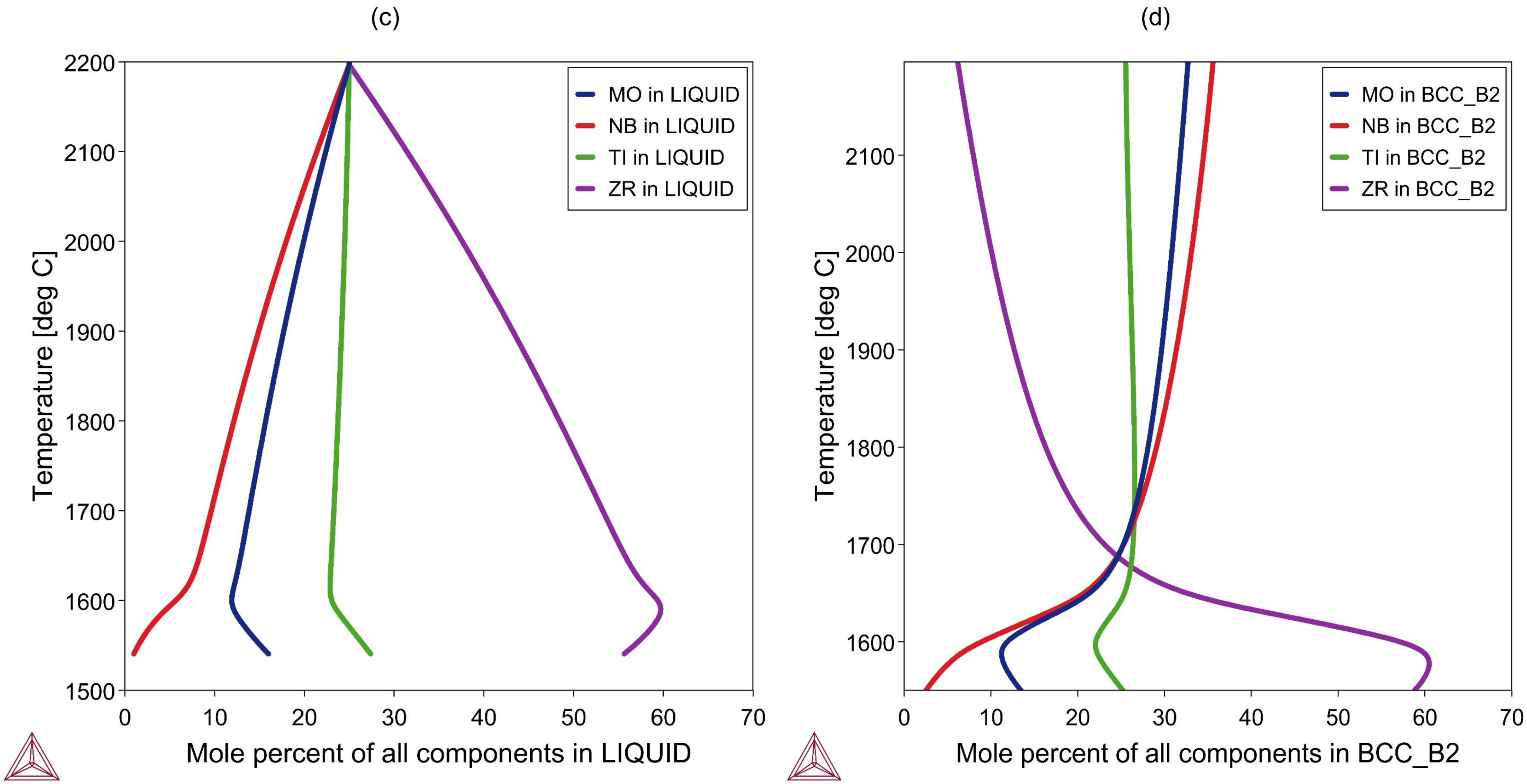


CALPHAD modelling – DII MoNbTiZr



CALPHAD modelling summary

	System	Equilibrium diagram	NE diagram	Microstructure
D I	MoNbTi	BCC + HCP	BCC	More or less homogeneous
D II	MoNbTiZr	BCC1 + BCC2 + HCP1 + C15 + HCP2	BCC	Zr segregation
D III	MoNbTiCr	BCC1 + C14 + C15 + BCC2	BCC+C14	Cr segregation in BCC + Cr_2Ti Laves
D IV	MoNbTiV	BCC1 + BCC2	BCC	V segregation
D V	MoNbTiAl	BCC1 + A15 + O phase + AlTi + Al_3Ti + BCC2	BCC+Al_3Ti	Al segregation in BCC
D VI	MoNbTiZrV	BCC1 + BCC2 + C15 + HCP1 + BCC2 + HCP2	BCC1 + BCC2	Zr & V segregation in BCC
D VII	MoNbTiCrV	BCC1 + BCC2 + HCP	BCC	Cr & V segregation in BCC
D VIII	MoNbTiCrAl	BCC1 + C14 + A15 + BCC2 + C15	BCC + C14	Al & Cr segregation in BCC + Cr_2Ti Laves
D IX	MoNbZrCrAl	C14 + BCC	BCC + C14 + Al_2Zr_3	Zr segregation in BCC + Cr, Zr, Al rich Laves

Empirical parameters and equations

- $\Delta S_{mix} = \Delta S_{mix}^{conf} = -R\sum_{i=1}^{N} x_i \ln x_i$ Boltzmann's hypothesis [6]
- $\Delta H_{mix} = 4\sum_{i=1,i\neq j}^{N} \Delta H_{mix}^{ij} \; x_i x_j$ Regular solution model [7]
- $\delta = \sqrt{\sum_{i=1}^{N} x_i \left(1 - \frac{r_i}{\sum_{j=1}^{N} x_j r_j}\right)^2}$ Zhang [8]
- $\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|}$ Yang [9]
- $\Delta\chi = \sum_{i=1}^{N} x_i \left(1 - \frac{\chi_i}{\chi_a}\right) * 100$ Poletti [10]
- $\Lambda = \frac{\Delta S_{mix}}{\delta^2}$ Singh [11]

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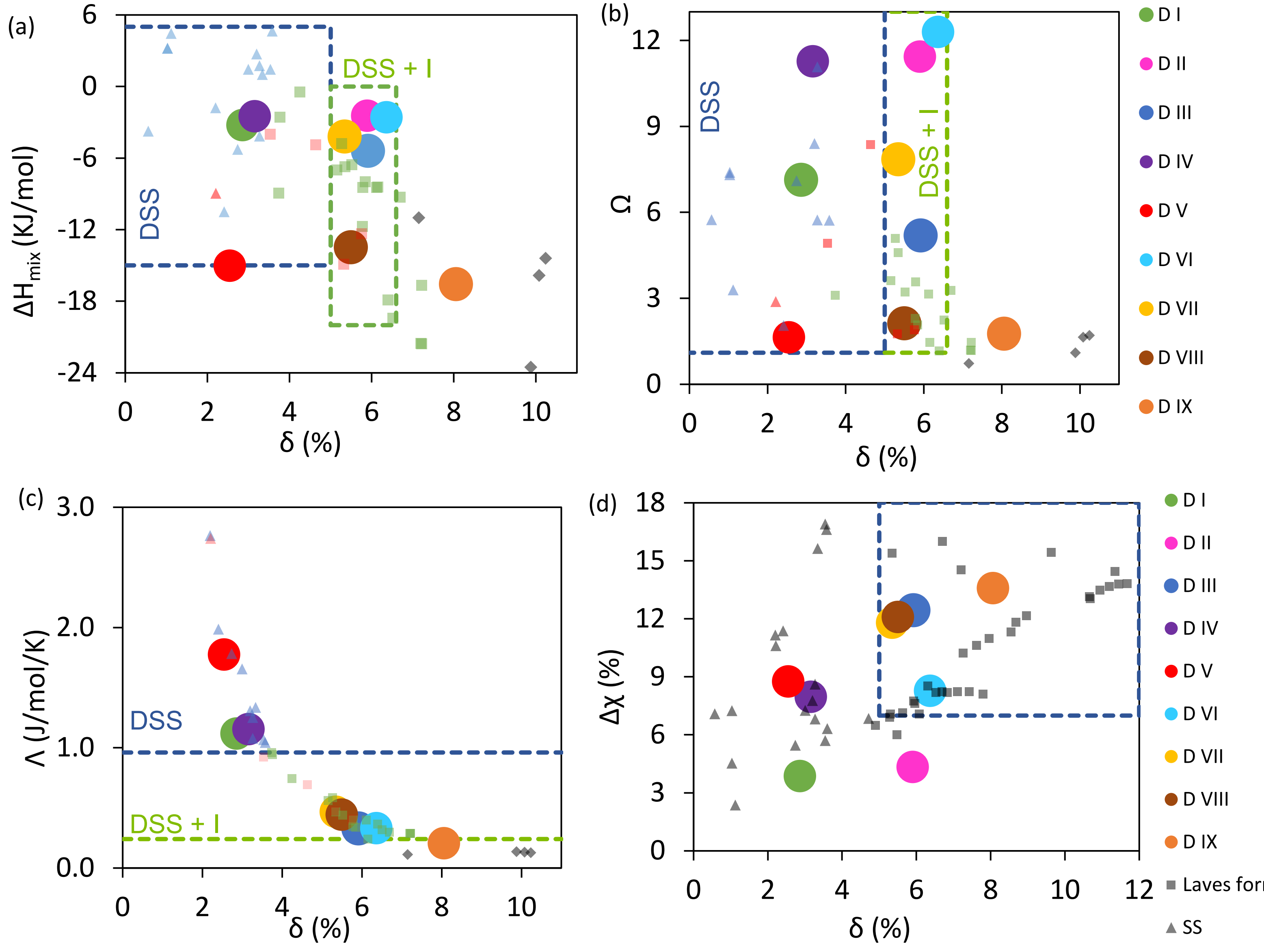
Calculated thermodynamic and empirical parameters

System	T_m [°C] average	ΔH_{mix} [KJ/mol]	ΔS_{mix} [J/K/mol]	Ω	δ [%]	Λ	Δχ [%]
D I	2256.00	-3.24	9.13	7.13	2.86	1.12	3.9
D II	2155.75	-2.45	11.53	11.43	5.90	0.33	4.3
D III	2156.25	-5.40	11.53	5.19	5.92	0.33	12.4
D IV	2169.50	-2.50	11.53	11.26	3.16	1.15	8.0
D V	1857.00	-15.03	11.53	1.63	2.55	1.77	8.8
D VI	2106.60	-2.59	13.38	12.29	6.37	0.33	8.3
D VII	2195.80	-4.21	13.38	7.85	5.35	0.47	11.8
D VIII	1867.00	-13.49	13.38	2.12	5.50	0.44	12.1
D IX	1904.40	-16.59	13.38	1.76	8.06	0.21	13.6

*41 additional equi-atomic systems from literature [11,12] were taken for constructing maps

Empirical value mapping & phase prediction

- Zhang's criteria
- Yang's criteria
- Singh's criteria
- Poletti's criteria



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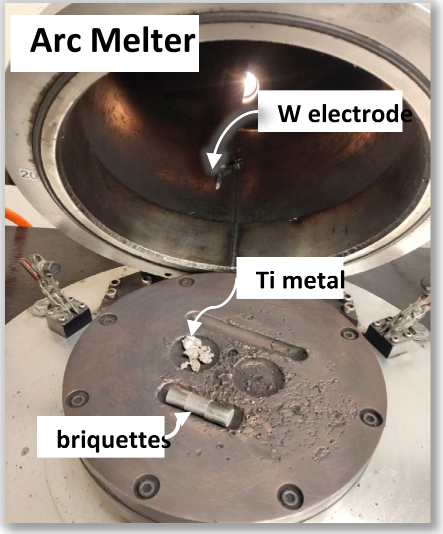
Empirical Modelling summary

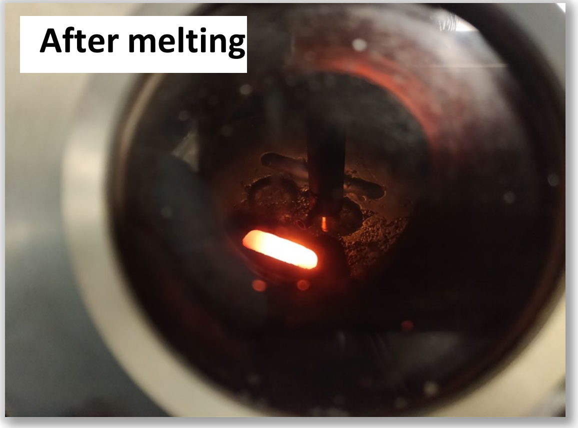
	System	Phase prediction
D I	MoNbTi	DSS
D IV	MoNbTiV	DSS
D V	MoNbTiAl	DSS
D II	MoNbTiZr	DSS + I
D III	MoNbTiCr	DSS + I
D VI	MoNbTiZrV	DSS + I
D VII	MoNbTiCrV	DSS + I
D VIII	MoNbTiCrAl	DSS + I
D IX	MoNbZrCrAl	I

Elements	r [Å]
Mo	1.363
Nb	1.429
Ti	1.462
Zr	1.600
Cr	1.249
V	1.340
Al	1.432

Fabrication

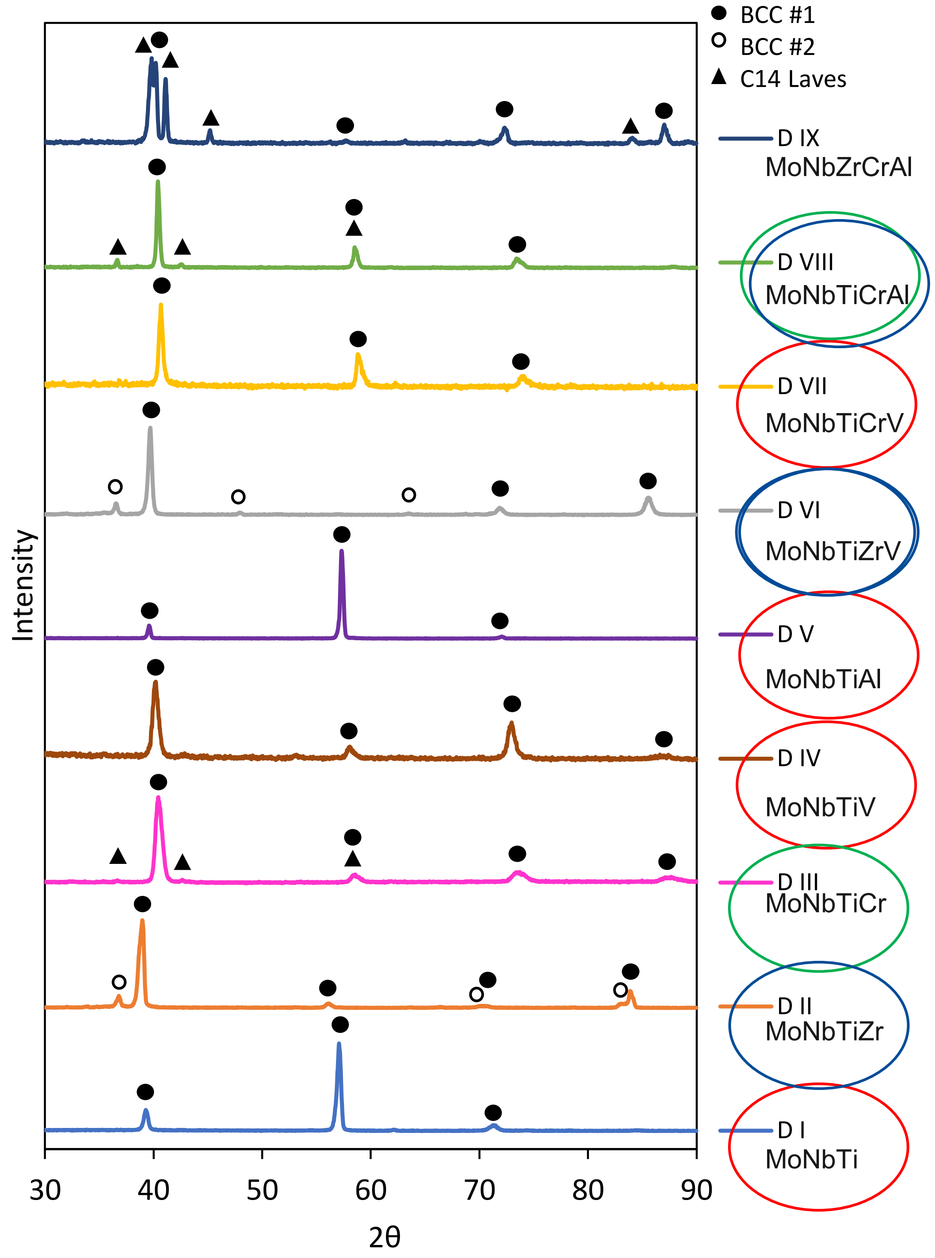
Powder





XRD for validation of modelling

- Consistent with NE CALPHAD predictions
- Agreement with empirical modelling
  - Single phase → D I, D IV, D V
  - SS + I → D III, D VIII
- Disagreement →
  - D II, D VI and D VII – intermetallics predicted
  - Laves phase prediction for D VI



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Chemistry, density and hardness of as-cast

- Chemistry –
  - within ±2% error from the nominal
- Hardness –
  - Lave phase detected D III, D VIII and D IX – higher
  - Lowest in D IV
- Density –
  - Close to estimated values by rule of mixture
  - Al containing – lower densities

	At %	Mo	Nb	Ti	Zr	Cr	V	Al
D I	Nominal	33.3	33.3	33.3				
	EDS	34.3	33.7	32.1				
D II	Nominal	25.0	25.0	25.0	25.0			
	EDS	24.0	24.2	26.4	25.3			
D III	Nominal	25.0	25.0	25.0		25.0		
	EDS	25.7	25.7	24.6		24.1		
D IV	Nominal	25.0	25.0	25.0			25.0	
	EDS	24.9	24.9	25.6			24.6	
D V	Nominal	25.0	25.0	25.0				25.0
	EDS	25.7	26.2	24.2				23.9
D VI	Nominal	20.0	20.0	20.0	20.0		20.0	
	EDS	19.4	19.7	20.6	19.9		20.4	
D VII	Nominal	20.0	20.0	20.0		20.0	20.0	
	EDS	18.1	20.9	18.2		21.7	21.1	
D VIII	Nominal	20.0	20.0	20.0		20.0		20.0
	EDS	20.0	20.8	18.7		20.5		20.0
D IX	Nominal	20.0	20.0		20.0	20.0		20.0
	EDS	21.2	21.[illegible]		19.[illegible]	18.9		19.0

System	Bulk Density [g/cm³]		Vickers Hardness
	Theoretical	Measured	
D I - MoNbTi	7.68	7.83	496.1
D II - MoNbTiZr	7.31	7.47	541.6
D III – MoNbTiCr	7.59	7.62	611.2
D IV – MoNbTiV	7.35	7.22	472.2
D V – MoNbTiAl	6.47	6.64	581.8
D VI – MoNbTiZrV	7.13	7.08	538.1
D VII - MoNbTiCrV	7.32	7.34	579.2
D VIII - MoNbTiCrAl	6.56	6.82	656.1
D IX - MoNbZrCrAl	6.97	6.98	820.6

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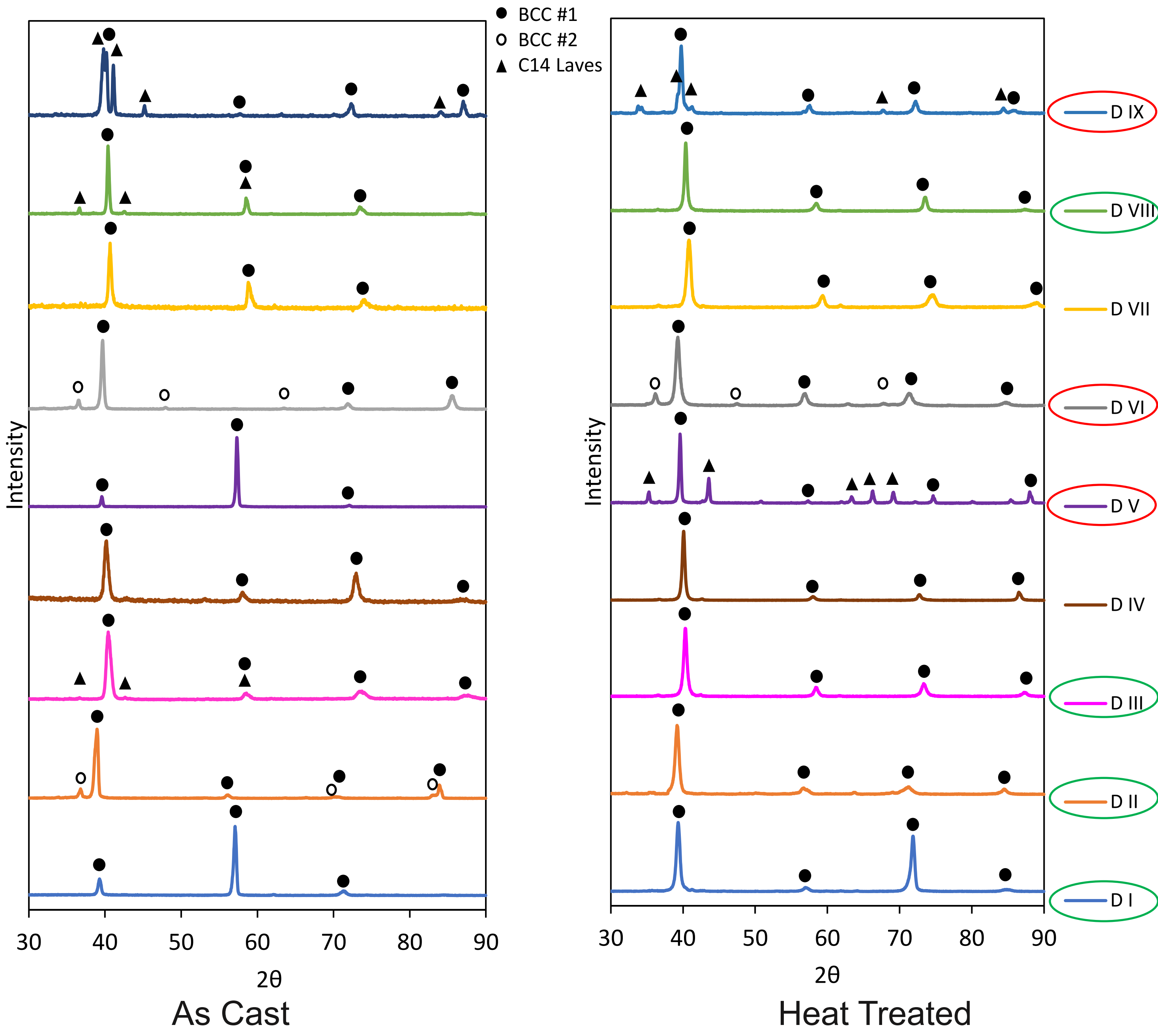
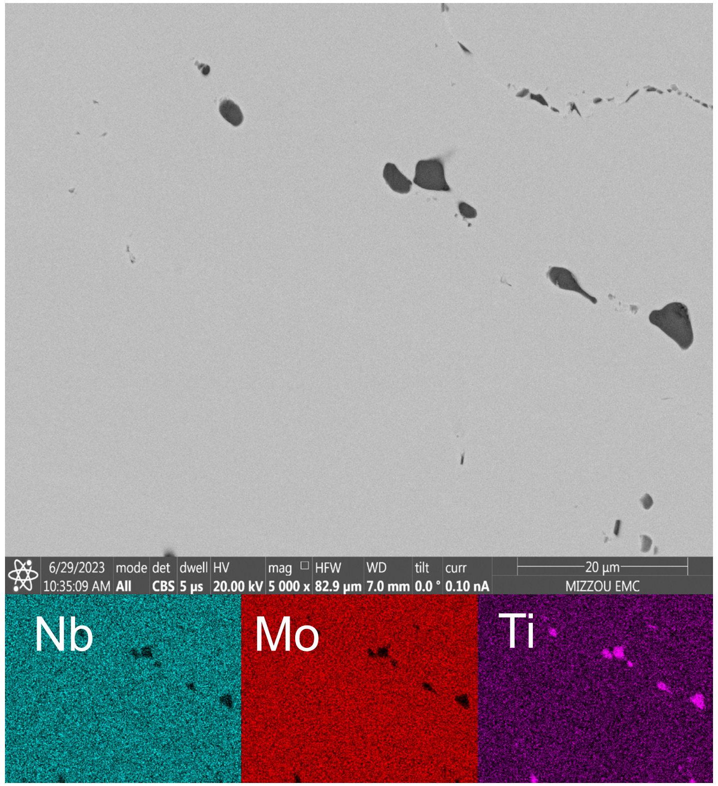
Heat treatment

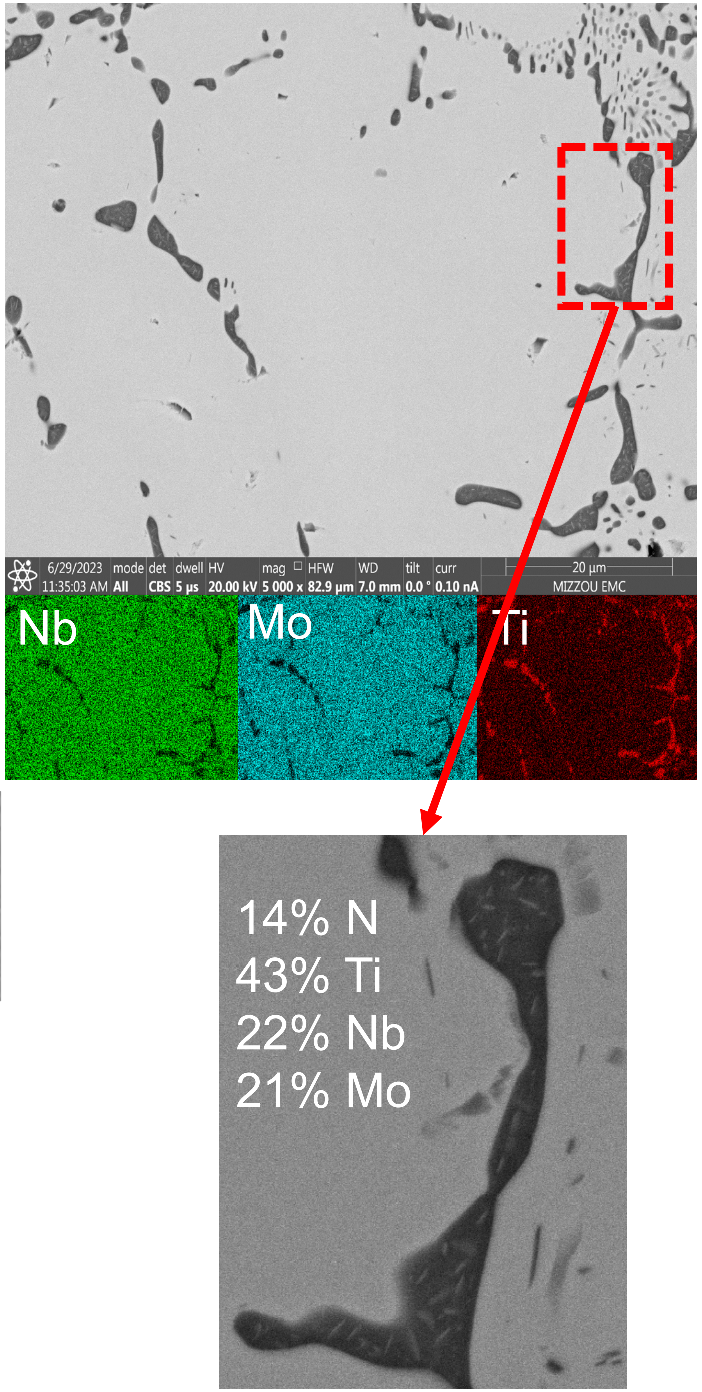
- 1500 °C for 24hr and water quenching
- D I retained single phase
- D II, D III, D VIII converted to single phase
- D V converted to multi phase
- D VI, DIX retained multiphase
- Heat treatment → homogenization, systems moving towards equilibrium

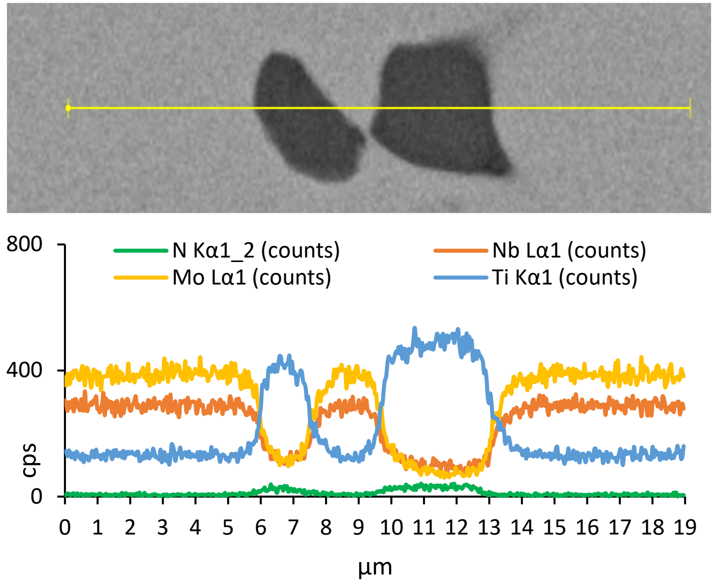


Microstructural analysis – D I - MoNbTi

- As cast – Single phase matrix + black Ti rich phase
- Heat treated– Single phase matrix + black Ti rich phase
- Ti rich phase – nitrides of Ti
  - ~ 28-30 at% N,   65-70 at% Ti with traces of Nb, Mo
- Needle like precipitates rich in Nb and Mo found co precipitated inside nitrides

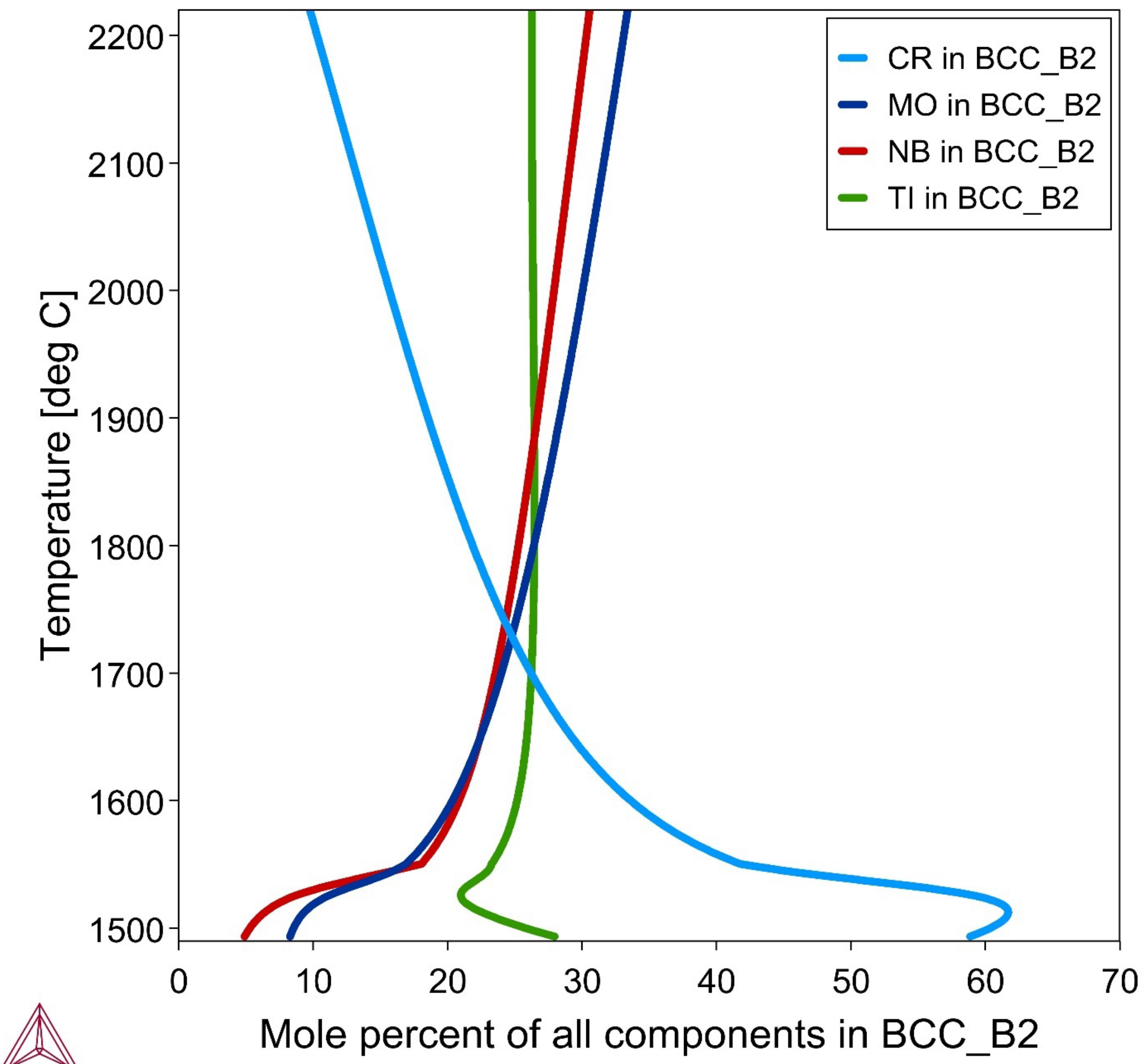


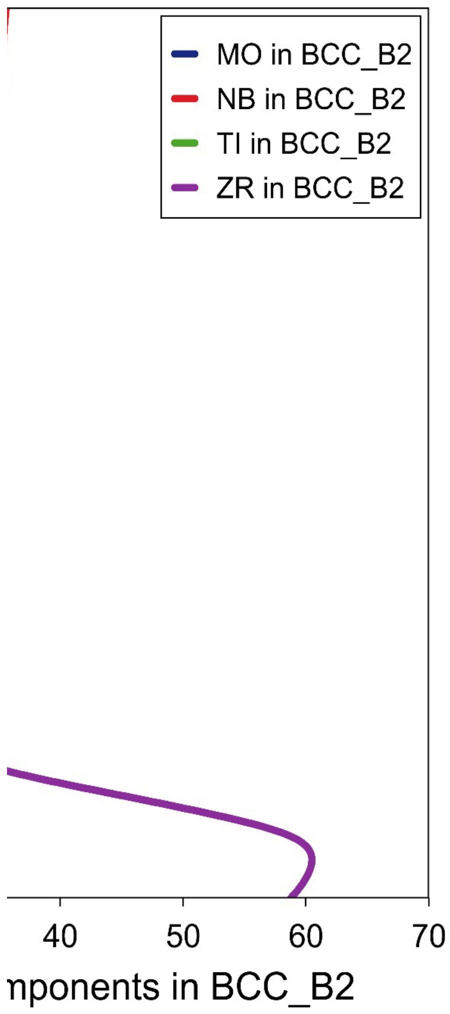




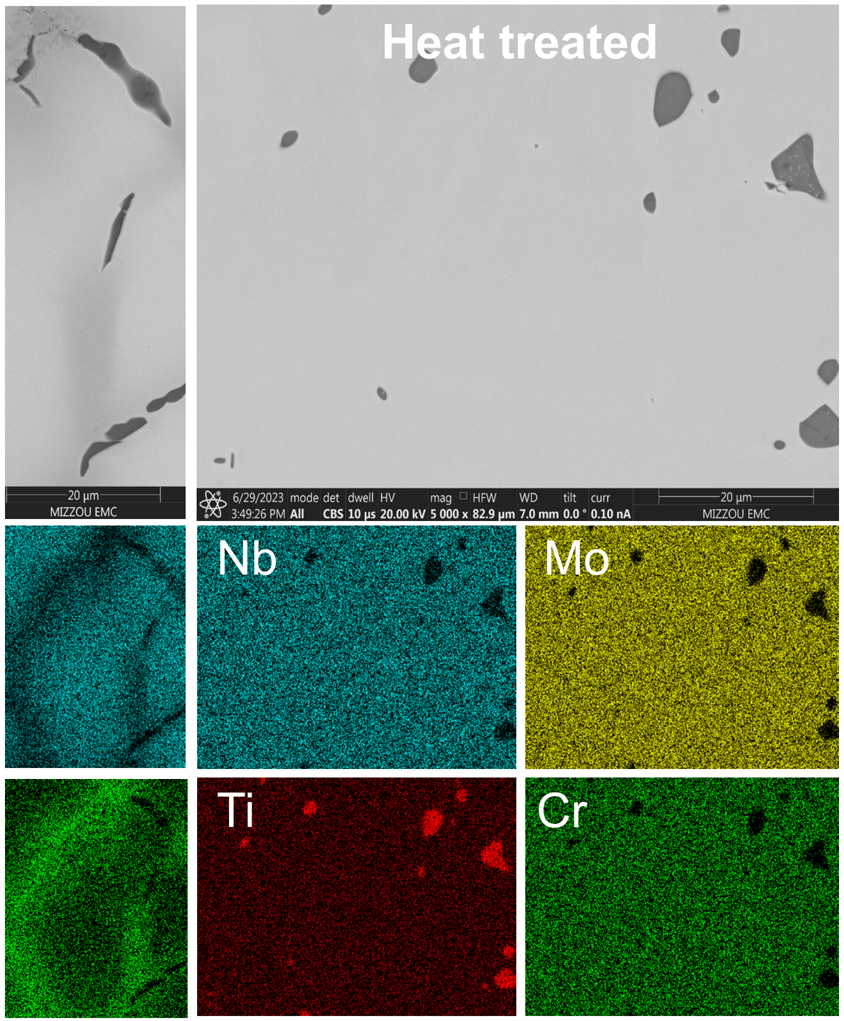
Microstructural analysis

(d)





D III - MoNbTiCr

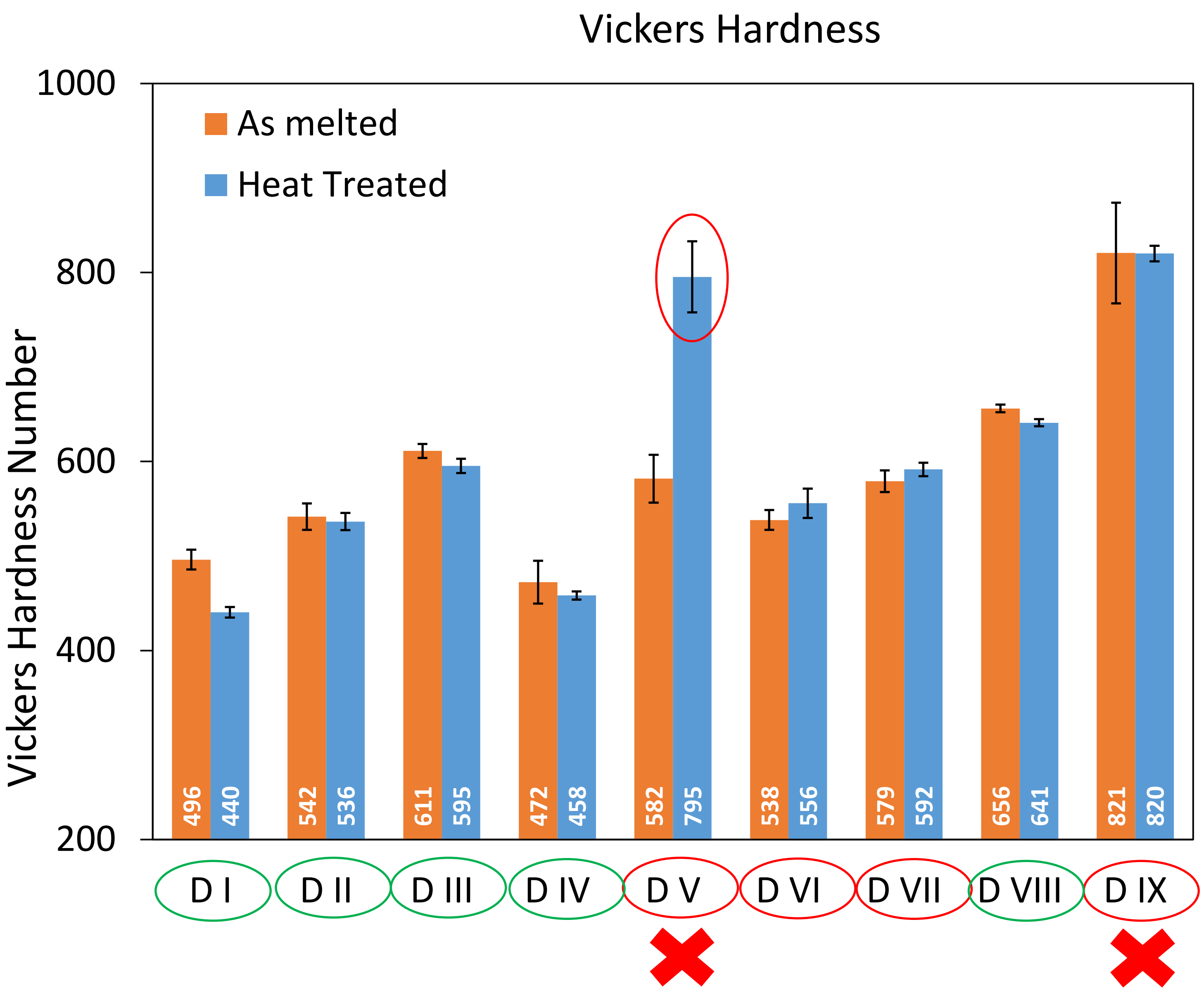


Microstructural analysis –

	System	As cast	Heat treated
D I	MoNbTi	Single phase matrix + Ti nitrides	Single phase matrix + Ti nitrides
D II	MoNbTiZr	Intergranular Zr and Ti enrichment + Ti, Zr nitrides	Single phase matrix + Ti, Zr nitrides
D III	MoNbTiCr	Intergranular Cr and Ti enrichment + Ti nitrides	Single phase matrix + Ti nitrides
D IV	MoNbTiV	Intergranular V and Ti enrichment + Ti nitrides	Single phase matrix + Ti nitrides
D V	MoNbTiAl	Single phase matrix + Ti nitrides	Multi-phased → Ti Nitrides + Ti rich phase + Nb, Mo rich phase
D VI	MoNbTiZrV	Intergranular Zr enrichment + Mo, Nb, V, Ti rich matrix + Zr rich precipitates	Reduced segregation, Zr rich GBs + Zr rich precipitates
D VII	MoNbTiCrV	Intergranular Cr and Ti rich GBs + Ti nitrides	Reduced segregation, Cr rich Intergranular + Ti Nitrides
D VIII	MoNbTiCrAl	Cr and Ti rich regions + Ti nitrides	Single phase matrix + Ti nitrides
D IX	MoNbZrCrAl	Nb, Mo rich phase + Al, Cr, Zr rich matrix	Nb, Mo rich phase + Al, Cr, Zr rich matrix

Hardness comparison

- Hardness
  - ↑multi phased systems → DV, D VI, D VII, D IX
  - ↓ attained/retained the single phase → D I, D II, D III, D IV, D VIII
  - Scatter of hardness values ↓ except for D V
  - D V, D IX – high hardness, multi-phased microstructure, machining difficulty due to brittleness – no further analysis

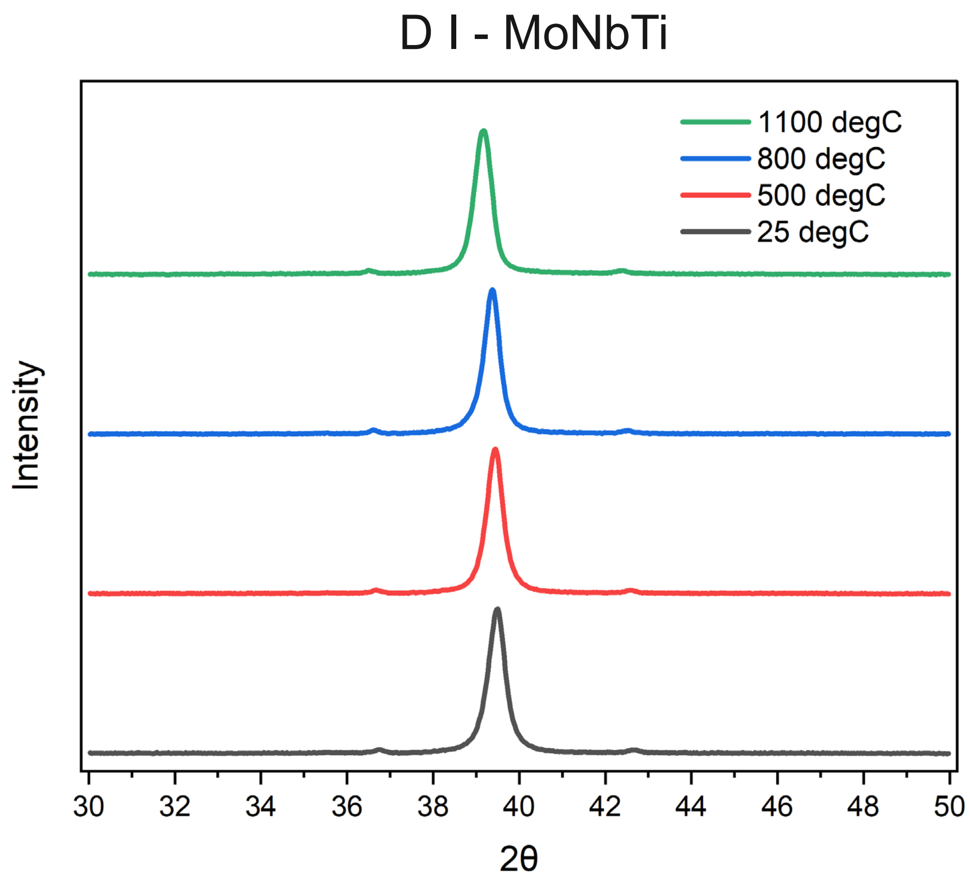


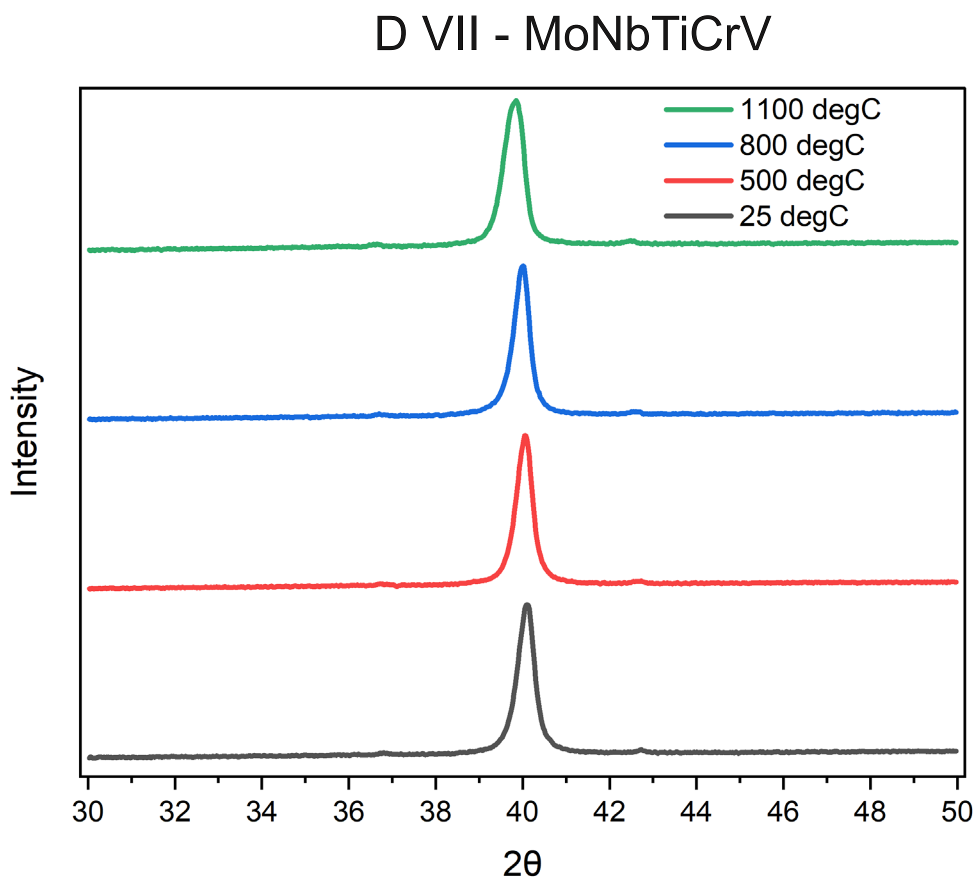
High temperature phase evaluation

- Evaluate phase stability at temperature range of interest –
  - 500 – 1000 ^{o}C (Gen IV reactor operation)
- High temperature XRD -
  - Performed in vacuum at 500, 800 and 1100 ^{o}C
- Dilatometry -
  - 10 ^{o}C/min heating of sample until 1050 ^{o}C followed by cooling at same rate
  - Change in length of specimen recorded every 0.05s
- Ageing studies -
  - Performed at 800 and 1000 ^{o}C for 48 and 96hrs
  - Microstructural analysis

High Temperature XRD

- No systems evidently showed peaks corresponding to new phases.

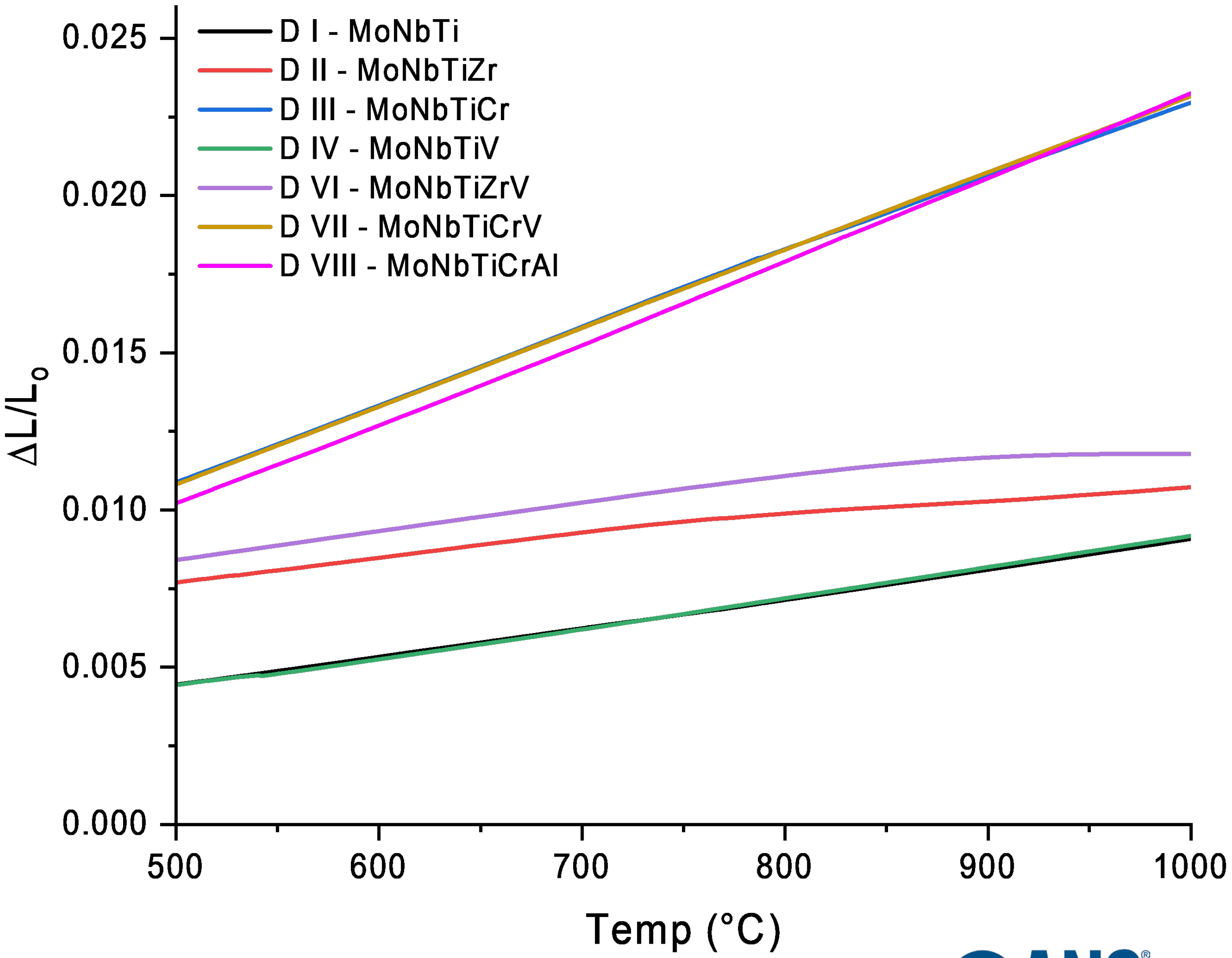




Dilatometry

- D I & DIV - lower CTE value compared to SS 304L and 316L
- Cr containing D III, D VI & D VIII - higher CTE value
- Zr containing D II and D VI changes slope around 800ºC.
- All others demonstrate phase stability at high temp

	System	CTE (/ºC)	Slope change
D I	MoNbTi	8.88 x10^{-6}	
D II	MoNbTiZr	7.86 x10^{-6}	→ 4.05 x10^{-6}
D III	MoNbTiCr	23.70x10^{-6}	
D IV	MoNbTiV	8.94 x10^{-6}	
D VI	MoNbTiZrV	8.75 x10^{-6}	→ 1.25 x10^{-6}
D VII	MoNbTiCrV	24.20 x10^{-6}	
D VIII	MoNbTiCrAl	24.50 x10^{-6}	
SS	314L	17.20 x10^{-6}	
SS	304L	17.30 x10^{-6}	



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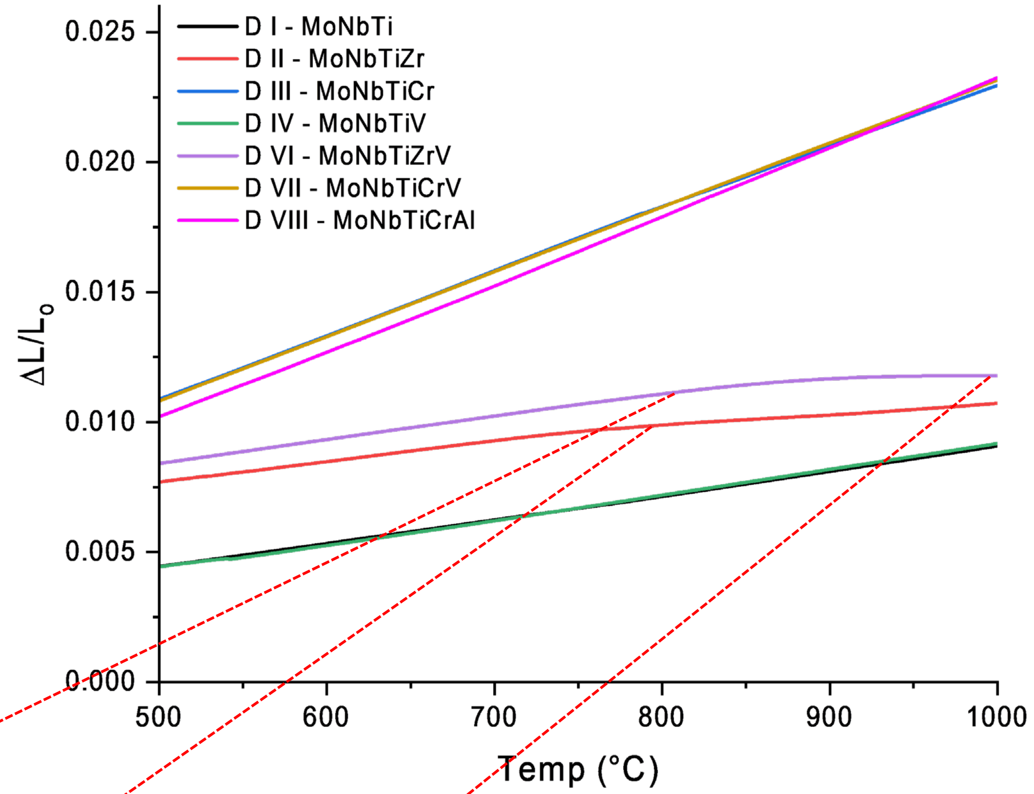
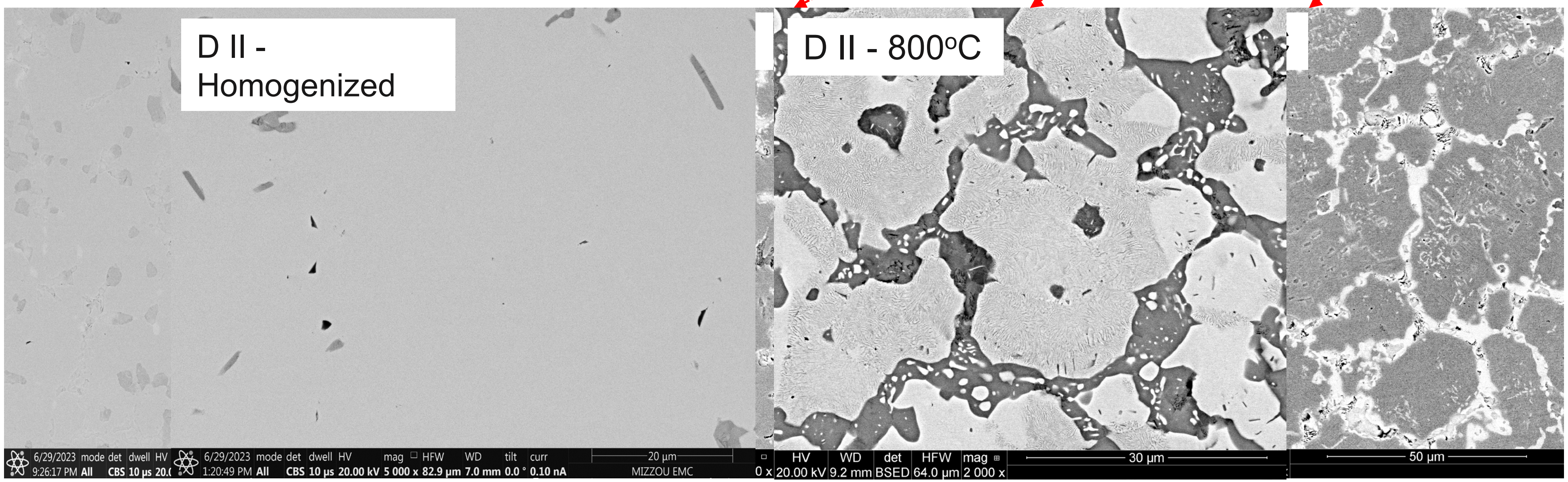
Dilatometry and Ageing studies

- Zr containing D II and D VI changes slope around 800°C.

	System	CTE (/°C)	Slope change
D VI	MoNbTiZrV	8.75 $\times 10^{-6}$	1.25 $\times 10^{-6}$
D II	MoNbTiZr	7.86 $\times 10^{-6}$	4.05 $\times 10^{-6}$

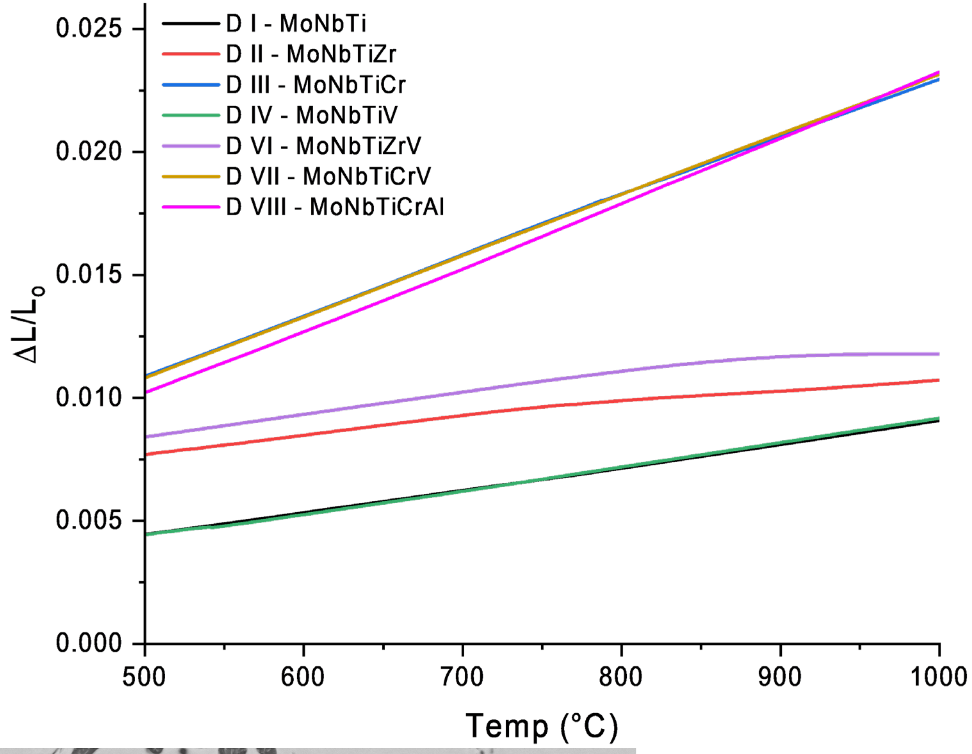


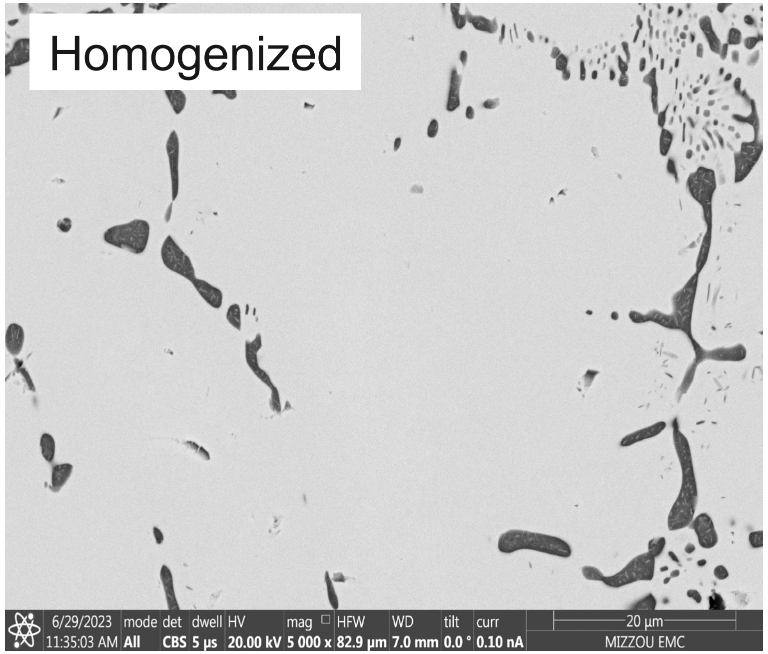
D VI – Homogenized →start of experiment

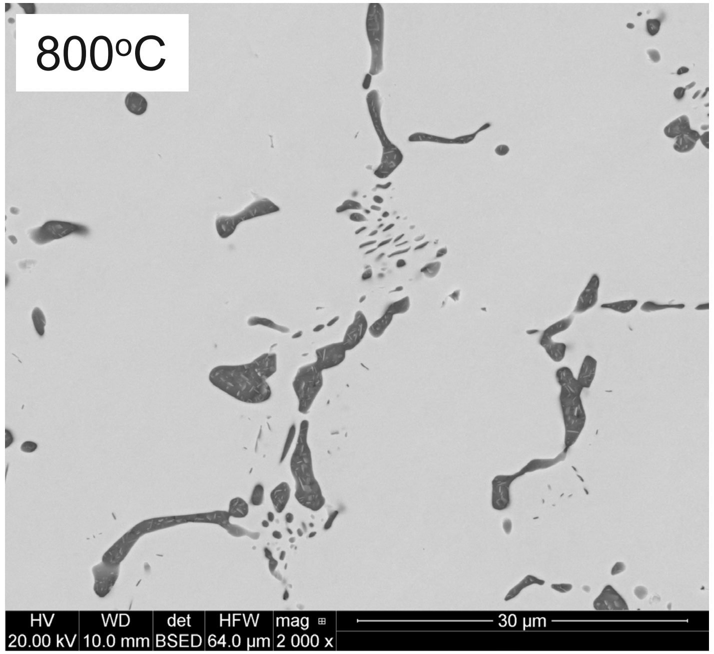


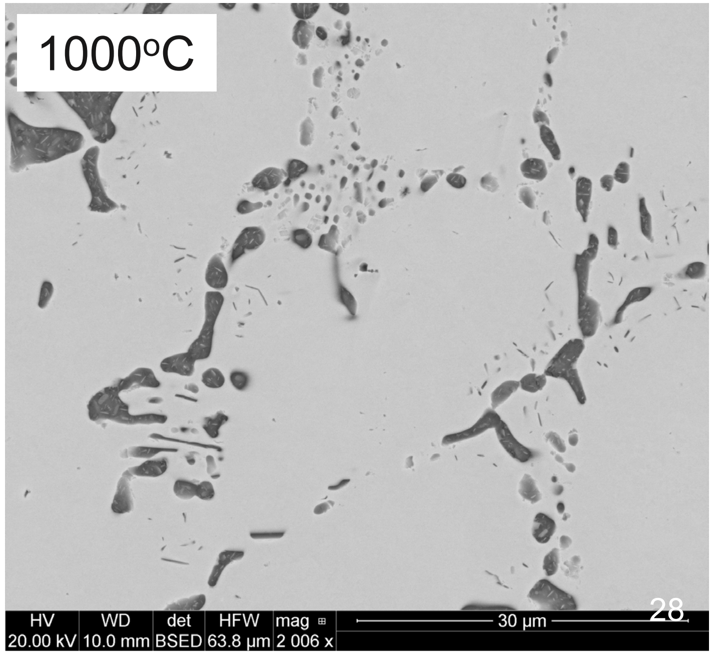
Dilatometry and Ageing studies

- All others D I, D IV and D III, D VII & D VIII – no major slope changes → phase stability at high temp
- Eg – D I – MoNbTi.









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Conclusions and future works

- Promising microstructural and dimensional stability in the operational range of Gen IV reactors.
  - D I – MoNbTi,
  - D III – MoNbTiCr,
  - D IV – MoNbTiV,
  - D VII – MoNbTiCrV,
  - D VIII – MoNbTiCrAl
- D II – MoNbTiZr, D VI – MoNbTiZrV although showed homogenized microstructure after heat treatment, dimensional and microstructural stability at higher temperatures → not promising.
- These materials are being irradiated in a reactor at INL, to evaluate their irradiation performance.
- Oxidation studies in steam and air are being carried out.
- More mechanical property testing need to be done before confirming their candidacy as structural materials in reactors.

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