



20th DISCUSSION MEETING ON THERMODYNAMICS OF ALLOYS
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BLED - SLOVENIA

Microstructural characterization of TaTiNbZr medium entropy alloy and in TaTiNbZrFe high entropy alloy produced by vacuum arc melting

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“Entropy does not work this
way”

C. G. Schön to F. Stein at a coffee break queue during the Intermetalics 2013 conference, after attending the presentation by Easo George on how the Cantor alloy decomposes after long time heat treatment, his answer was “I know”.

Medium entropy? High entropy?

- TiTaNbZr (TTNZ)

- All these elements conform the Hume-Rothery (HR) rules for solid solution
- The $\Delta S_{\text{mix}} \leq -R \cdot \ln(0,25) = 11.5 \text{ J mol}^{-1} \text{ K}^{-1}$
- “Medium-entropy”

- TiTaNbZrFe (TTNZF)

- Fe does not conform the the HR rules with the other components
 - Fe valence: +2 or +3
 - Fe radius: 0,122 nm
- The $\Delta S_{\text{mix}} \leq -R \cdot \ln(0,20) = 13.4 \text{ J mol}^{-1} \text{ K}^{-1}$
- “High-entropy”

Maximum solubilities of each element in each binary system

Solvent/Solute	Ta	Ti	Nb	Zr	Fe
Ta	-	100% (β)	100%	100% (β)*	8,6%
Ti	100% (β)	-	100% (β)	100% (α and β)	24,7% (β)
Nb	100%	100% (β)	-	100% (β)	9,7%
Zr	100% (β)*	100% (α and β)	100%	-	4%(β)
Fe	2,1%(δ)	9% (α)	5,2%(α)	1,2%(γ)	-

- ➔ The TTNZ alloy would be expected to present a single phase state, since all elements have complete solubility at high temperature in the binaries
- ➔ If the high-entropy effect would acts in the TTNZF system, this also should result in a single phase state

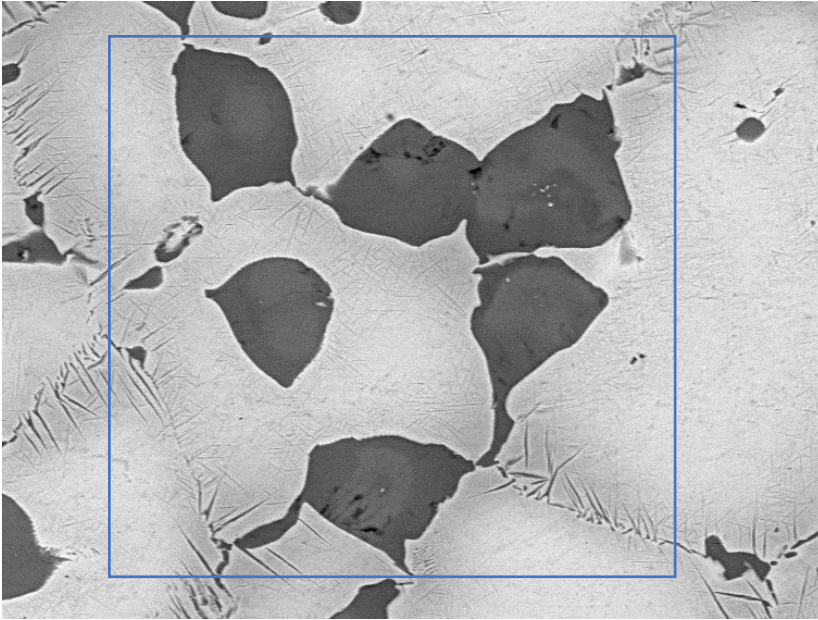
Experimental

- Commercially pure elements (99,9%)
- Vacuum arc melting: Four meltings turning upside down
 - 60V – 225 A – 10 to 15s each melt
 - Water cooled (room temperature 25°C to 35°C) copper base
 - Atmosphere: low pressure high purity argon
 - Cooling in situ to room temperature after each melting
- SEM – EDS
- XRD (Cu K α)

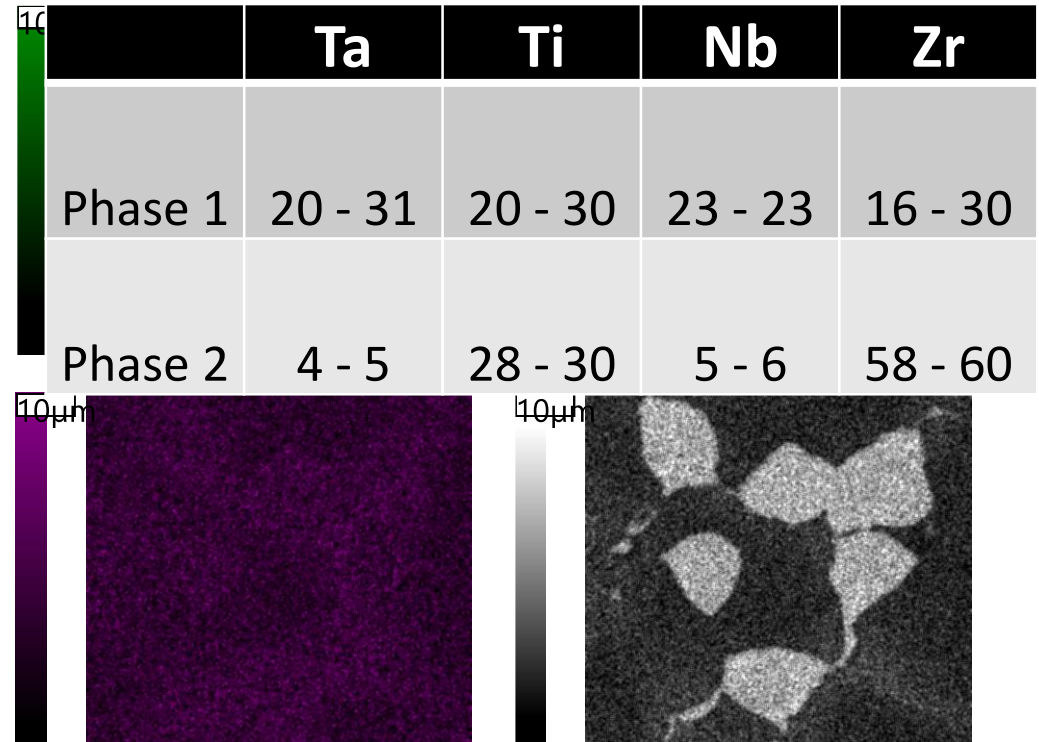
Heat treatment

- TTNZ - 1273 K (1000°C)
24h
 - Highest possible temperature on available equipments
 - Experimental limit (quartz encapsulation and muffle maximum working T)
- TTNZF – 1173K (900°C)
24h
 - To avoid a potential liquefaction due to eutectics
 - Low eutectic points in the binaries
 - FeZr: 928°C
 - FeNb: 1373°C
 - FeTa: 1442°C
 - FeTi: 1025°C

Results – TTNZ AC

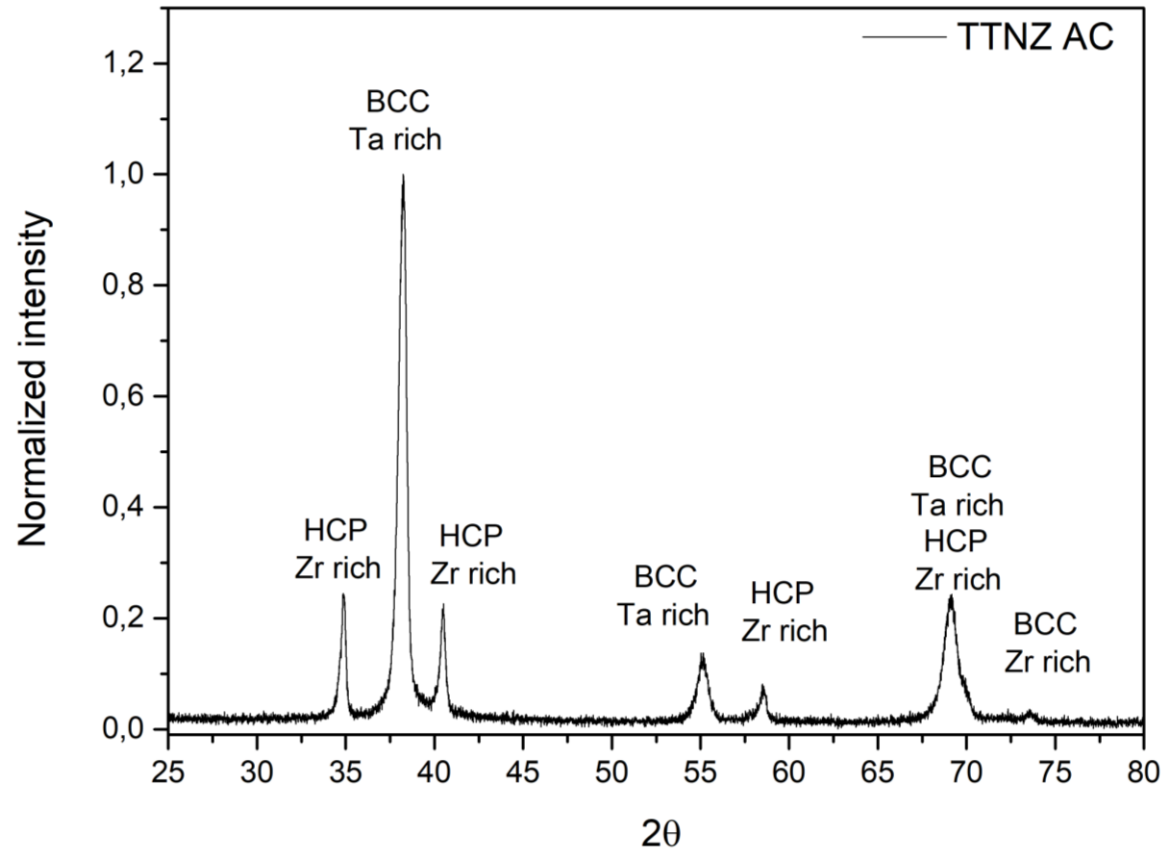


- ➔ Nb-La and Zr-La signals overlap during the mapping
- ➔ Severe Zr segregation
- ➔ Uniform Ti distribution



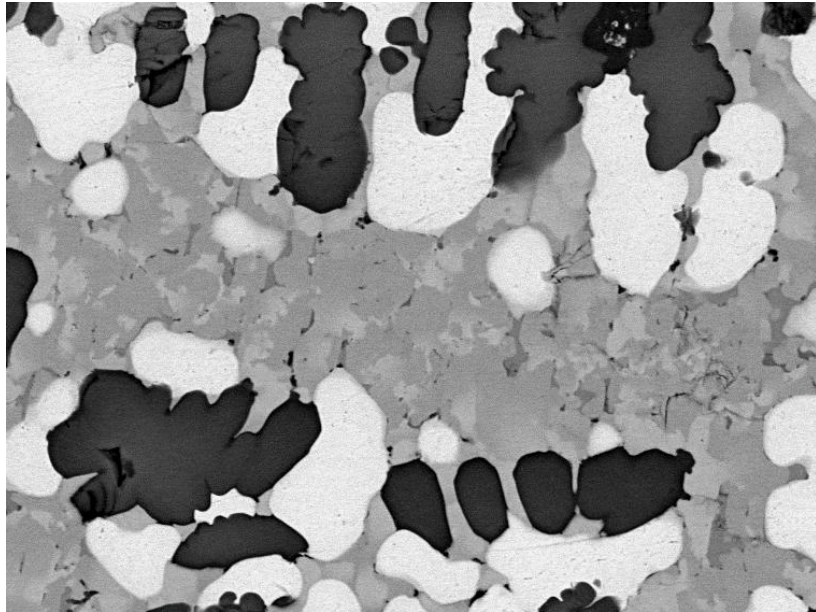
Ta

Results – TTNZ AC – XRD



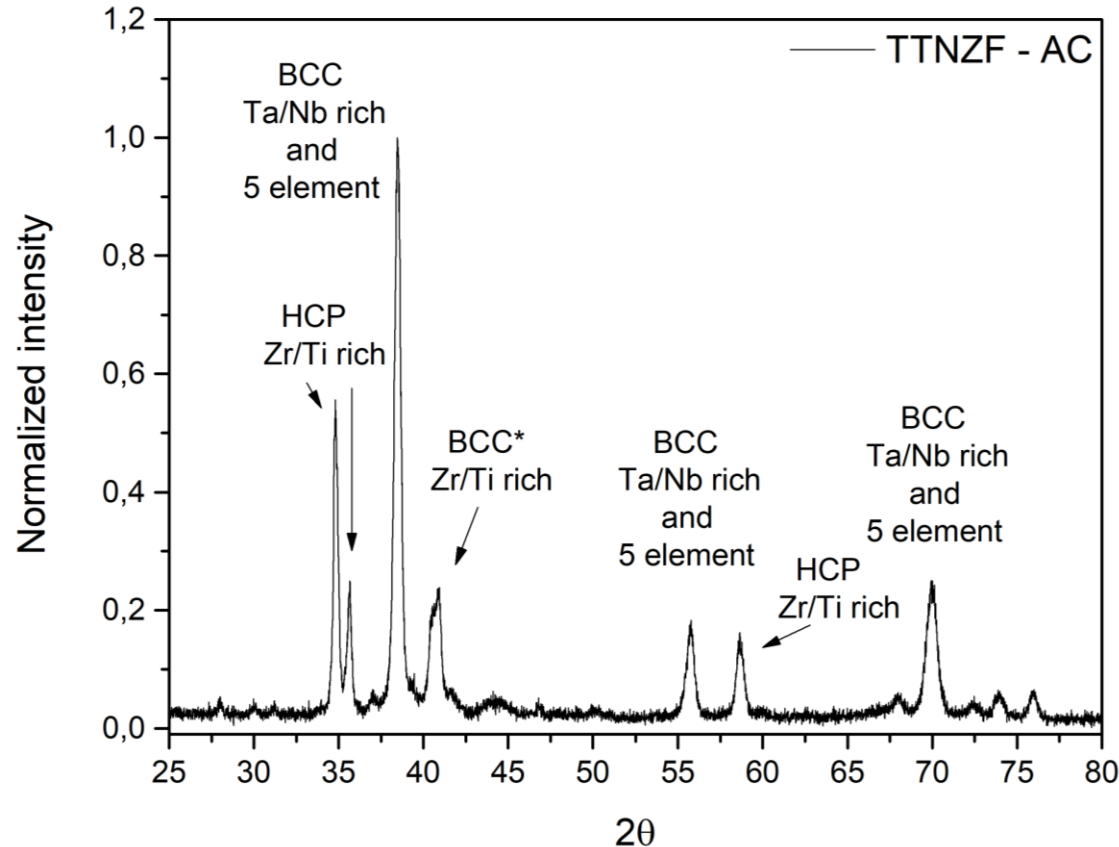
Phase 1  BCC Ta/Nb rich (β)
Phase 2  HCP Zr/Ti rich (α)

Results – TTNZF AC



	Ta	Ti	Nb	Zr	Fe
Phase 1	34 – 35	14 – 16	29 – 30	9 – 10	8 – 9
Phase 2	6 – 7	32 – 33	9 – 10	46 – 49	3 – 4
Phase 3	4 – 5	15 – 20	6 – 7	65 – 67	4 – 6
Phase 4	10 – 20	16 – 23	14 – 18	4 – 6	Fe-K

Results – TTNZF AC – XRD



Phase 1 BCC Ta/Nb rich (β_1)

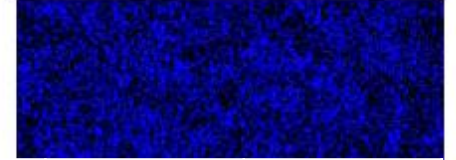
Phase 2 HCP Ti rich (α)

Phase 3 HCP Zr rich (β_2 ?)

- May result from phase transformation on cooling

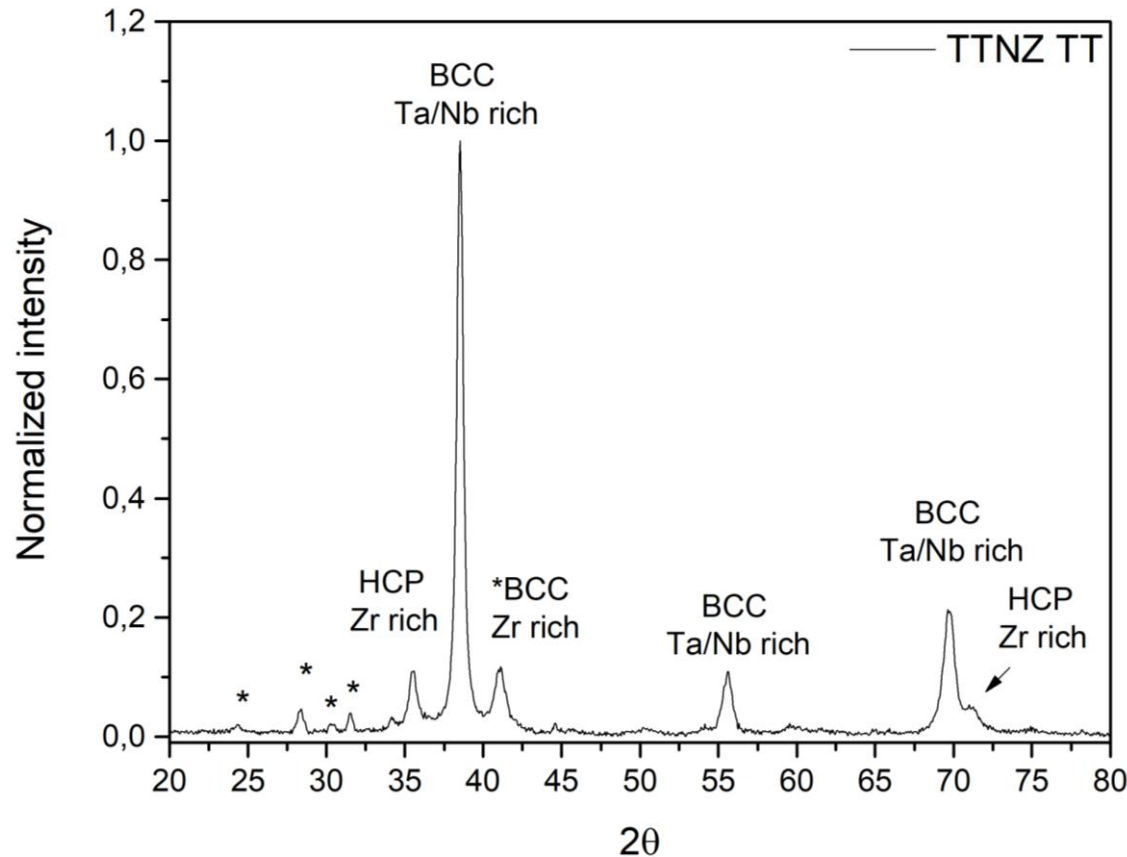
Phase 4 5 element BCC (β_3)

Results TTNZ HT – SEM+EDS



	Ta	Ti	Nb	Zr
Phase 1	55 – 62	5 – 8	25 – 26	7 – 10
Phase 2	20 – 21	19 – 22	13 – 14	43 – 45
Phase 3	10 – 11	4 – 6	7 – 8	74 – 75

Results – TTNZ HT – XRD



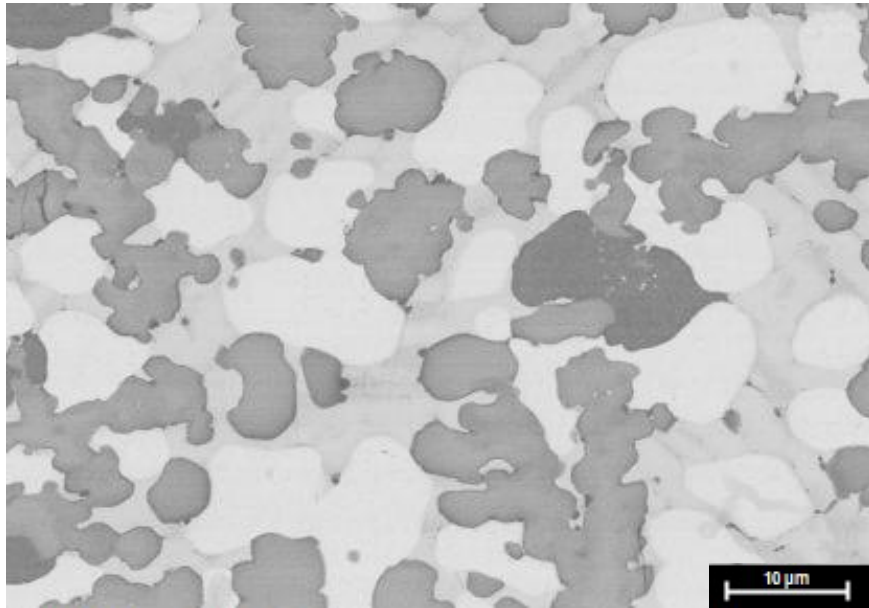
Phase 1 BCC Ta/Nb rich (β_1)

Phase 2 BCC Ti/Zr rich (β_2)

Phase 3 HCP Ti/Zr rich (α)

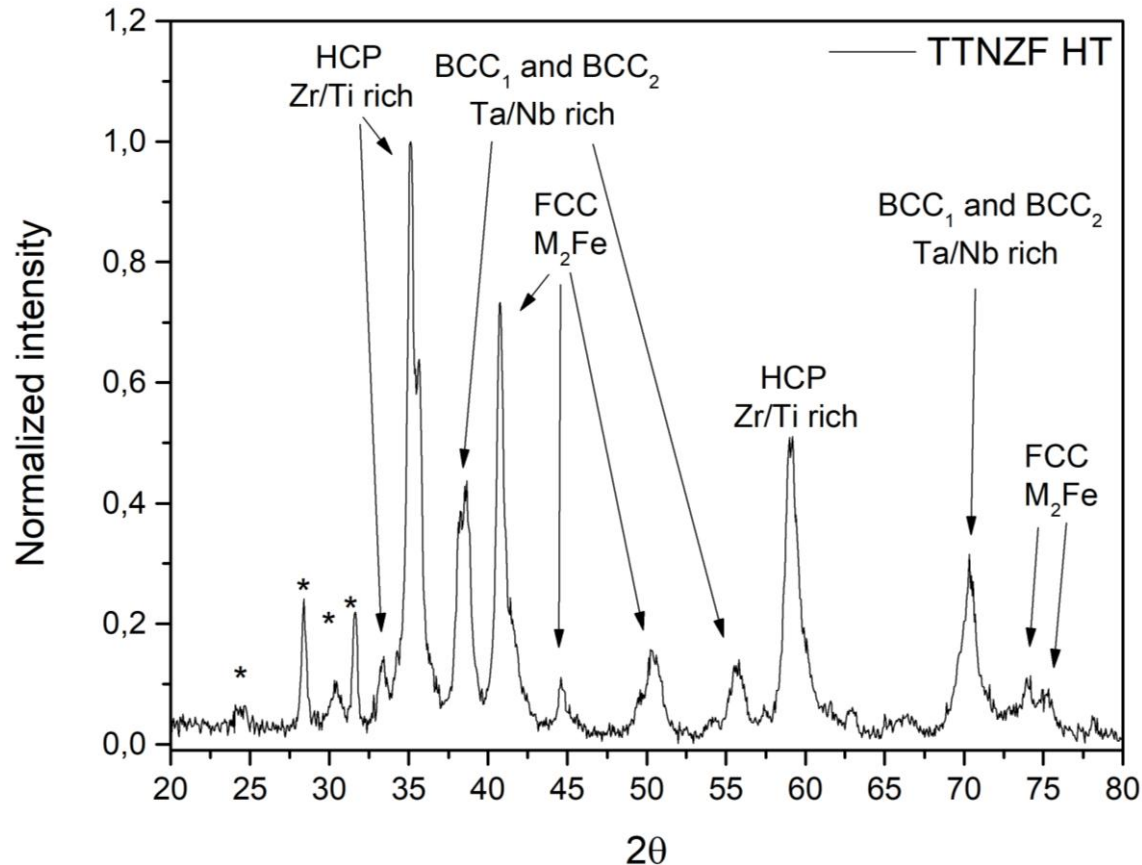
* ZrO_2

Results TTNZF HT – SEM+EDS



	Ta	Ti	Nb	Zr	Fe
Phase 1	34 – 35	13 – 14	31 – 32	9 – 10	8 – 9
Phase 2	25 – 26	19 – 20	29 – 30	18 – 19	6 – 7
Phase 3	8 – 8,5	35 – 37	11 – 12	36 – 38	4 – 5
Phase 4	21 – 22	12 – 14	21 – 22	8 – 9	34 – 35

Results – TTNZF HT – XRD



- Phase 1 BCC Ta/Nb rich
 - Phase 2 BCC Ti rich
 - Phase 3 HCP Ti/Zr rich
 - Phase 4 FCC M₂Fe (C15?)
- * ZrO₂

Conclusions

- What drives the thermodynamics of high-entropy alloys is... Metallurgy
- Both the TTNZ and the TTNZF alloys show a complex microstructure containing more than one phase, both in the As cast state and in the Heat treated condition
- There are indications of a three-phase miscibility gap in these systems (Morral's "rose diagram")