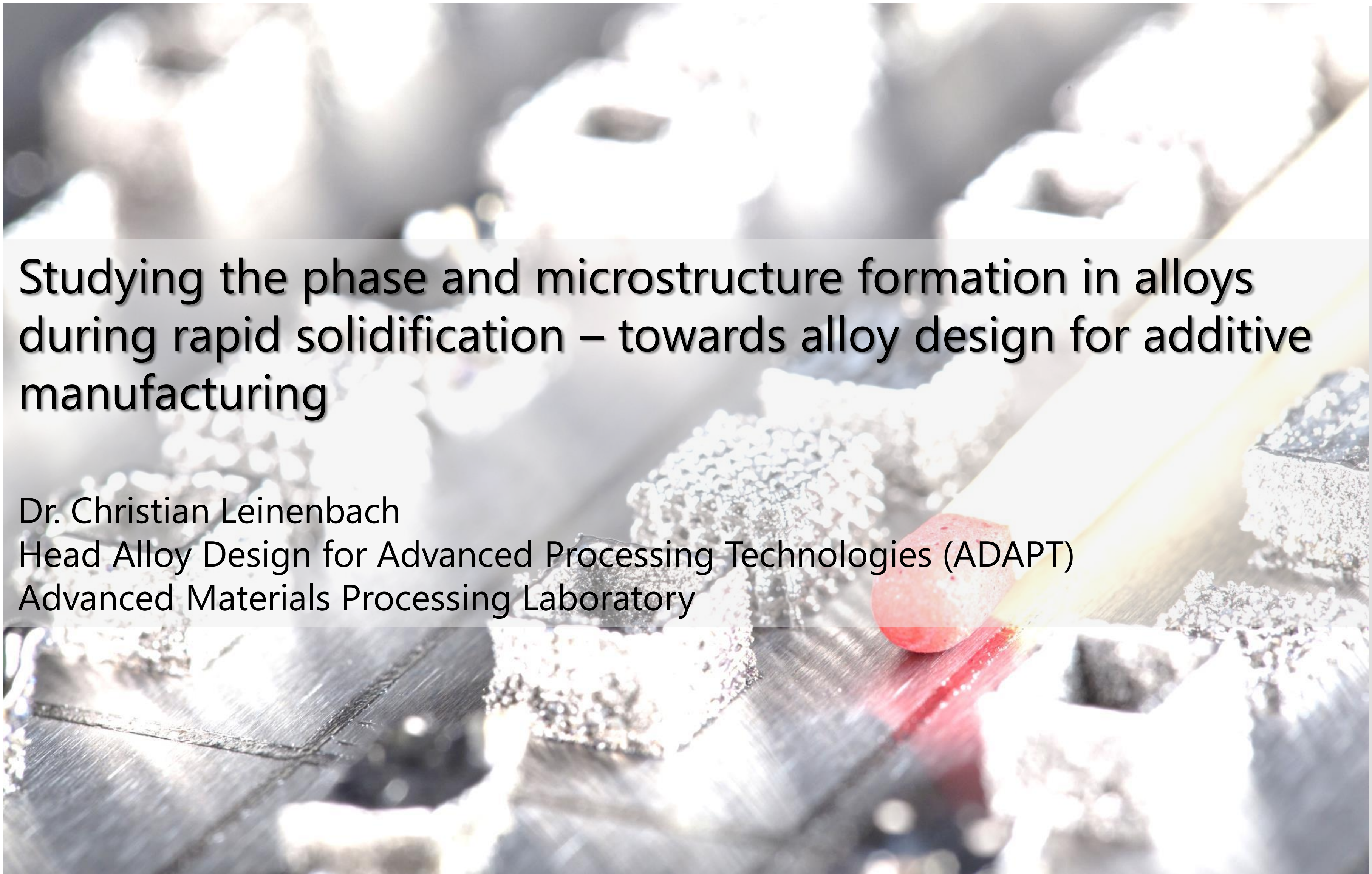
Willkommen
Welcome
Bienvenue



Studying the phase and microstructure formation in alloys during rapid solidification – towards alloy design for additive manufacturing

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Advanced Materials Processing Laboratory

Outline

- Materials aspects related to AM – some basics
- Development of an ODS-TiAl alloy for AM
  - Microstructure formation during rapid solidification
  - Microstructure of AM processed ODS-TiAl
- Development of bronze/diamond composites for AM
  - SLM processing of bronze/diamond composites
  - Rapid solidification of Cu-Sn-Ti alloys
- Summary and outlook

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Materials of interest for AM (in CH)

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- In Switzerland, there is a specific need for AM of the following materials
  - Advanced high-temperature alloys (γ'-hardening Ni-based alloys, Co-based alloys, TiAl) for power generation and aerospace applications
  - Tool steels, HSS, metal-superabrasives composites for advanced shape forming tools (grinding, cutting, milling etc.)
  - Precious metal alloys (Au-, Pd-, Pt-based) for jewelry and watches

➢ Useful information on the processability of those materials is very limited or not existing!

What are the problems with AM processing?

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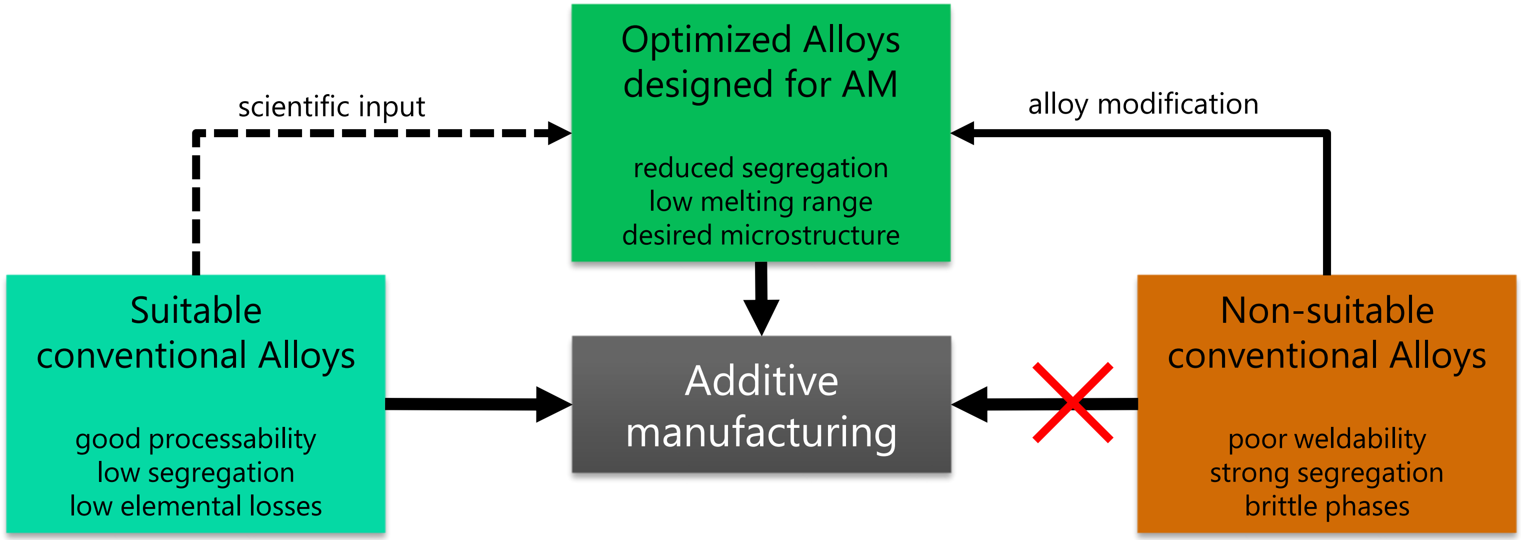
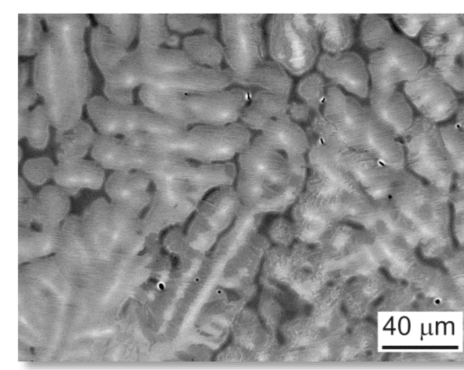


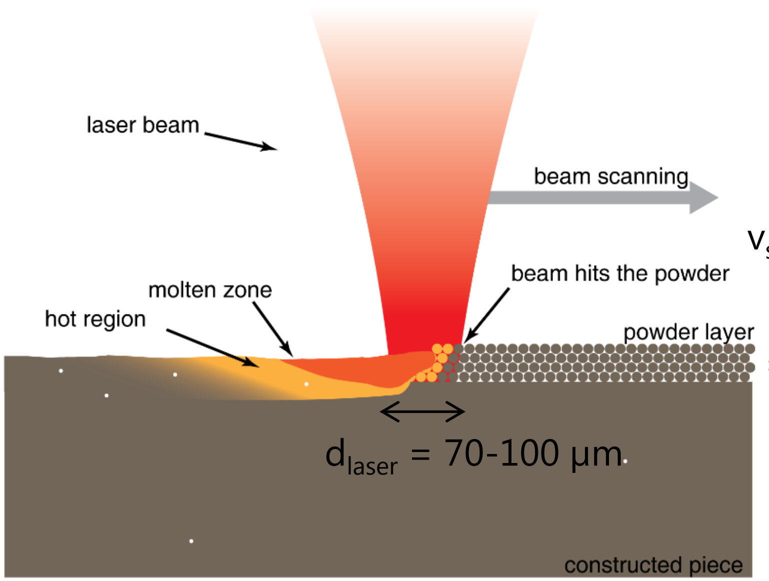
- typical problems in AM with non-suitable alloys:
  - hot cracking
  - strong segregation of specific elements
  - thermal cracking of brittle phases due to high stresses

  } alloy chemistry dependent

- *ex situ* studies on rapid solidified alloys
  - characterization of microstructure, phase analysis and segregation tendency
  - influence of alloying elements on behavior under AM conditions
  - screening of potential / already available / new alloys
- *in situ* studies to follow solidification and transformation



A look into the AM process conditions



v_{scan} = 100-3000 mm/s

d = 40-60 µm

Thermal penetration depth

$$l_{therm} = 2\sqrt{D\tau}$$

$$D = \frac{k}{\rho C_p} \qquad \tau = \frac{d_{laser}}{v_{scan}}$$

Example:
D_{steel} ≈ 4 mm^2/s
d_{laser} = 0.1 mm
v_{scan} = 1000 mm/s

→ l_{therm} = 40 µm

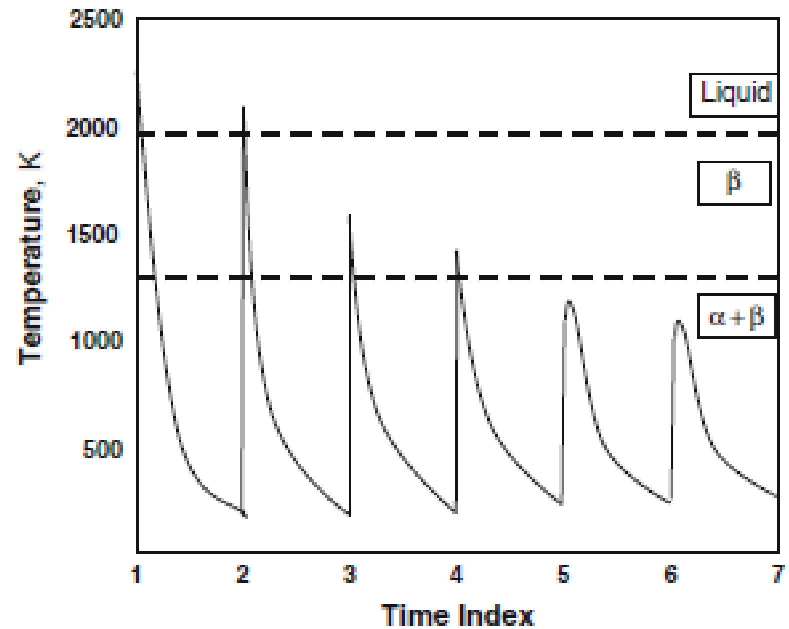
- A small material volume is rapidly heated and cooled with large thermal gradients ($\Delta T \approx 10^3$- 10^4 K/s)

→ The molten material solidifies very rapidly!

Thermal history during AM

- Charactistics of AM processing
  - Fast heating and cooling ($\Delta T \approx 10^4$ K/s)
  - → suppressed phase transformations; supersaturated phases
  - → segregation
  - → thermal residual stresses
  - Unidirectional heat flow into building plate/substrate
  - → textured grains; anisotropic properties
  - Every layer undergoes repeated heating and cooling cycles; temperatures can exceed T_{liq} or $T_{\alpha \leftrightarrow \beta}$
  - → Multiple phase transformations, complex microstructures with unwanted properties

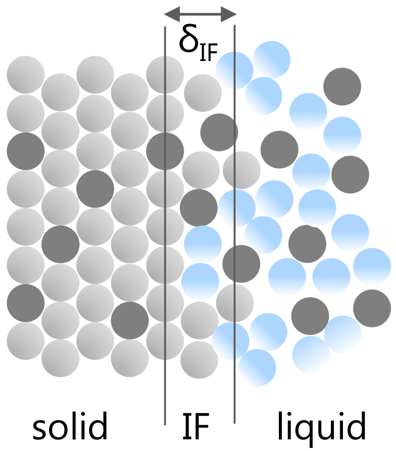
thermal profile of a single layer AM processed Ti-6Al-4V



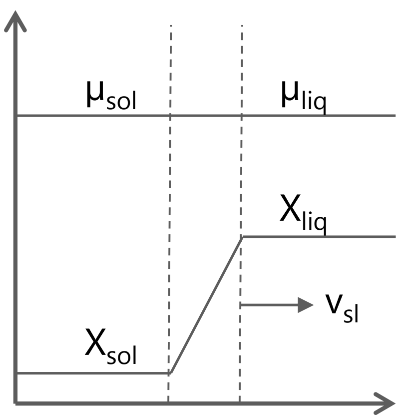
/W.E. Frazier, J. Mater. Eng. Perform. 23 (2014) 1917/

Solid-liquid interface: slow vs. rapid cooling

slow (equilibrium) cooling

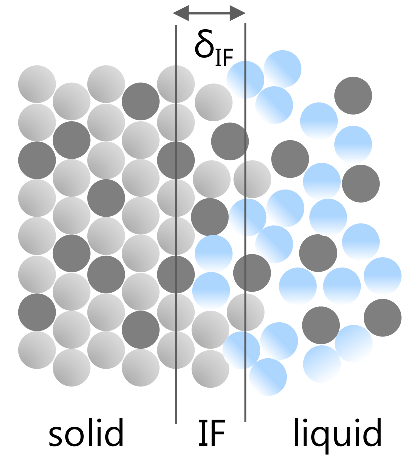


$$v_{sl} \ll \frac{D_{liq}}{\delta_{IF}}$$

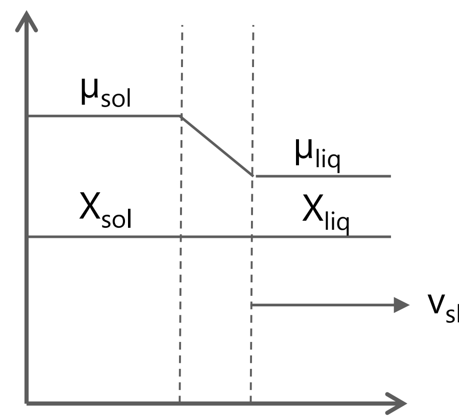


$$X_{sol} = k^m \cdot X_{liq}$$

rapid cooling

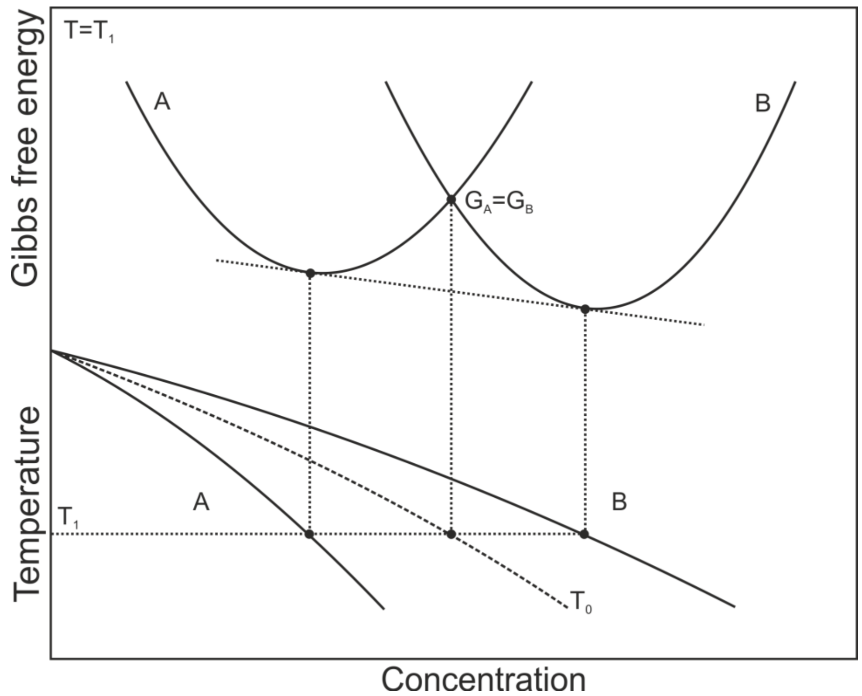


$$v_{sl} \geq \frac{D_{liq}}{\delta_{IF}}$$



$$X_{sol} > k^m \cdot X_{liq}$$

Non-equilibrium phase transformations



- equilibrium phase diagram
  - common tangent construction → energy minimization by formation of two phases
  - equilibrium composition of the formed phases at T_1
- diffusion-less phase transformations
  - ideally no diffusion → all phases have the same composition
  - T gives the composition at which G_A=G_B
  - a phase B transforms to A if G_A<G_B

Alloy development for AM – Empa approach

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- Ultimate test: AM using an optimized alloy
  - AM equipment
  - new alloy according to specifications
  - suitable powder shape

processability=f(process, powder, alloy)

- Intermediate test: Alloy behavior during rapid melting and cooling using the AM equipment
  - equipment for rapid heating and cooling (=AM equipment)
  - new alloy in solid form
  - no powder needed

«processability»=f(process, alloy)

- First level test: Alloy behavior at high cooling rates
  - rapid cooling equipment (≠ AM equipment)
  - new alloy
  - no powder needed

«processability»=f(alloy)

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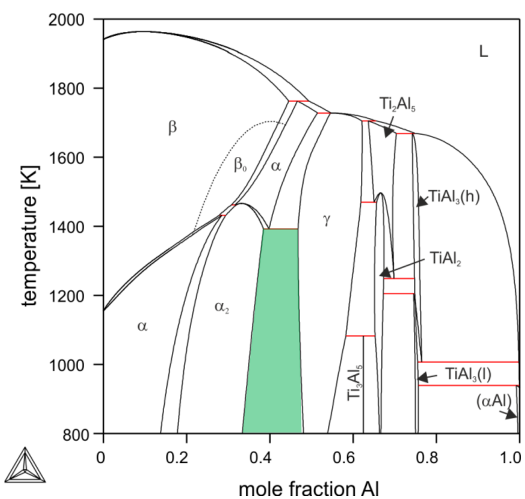
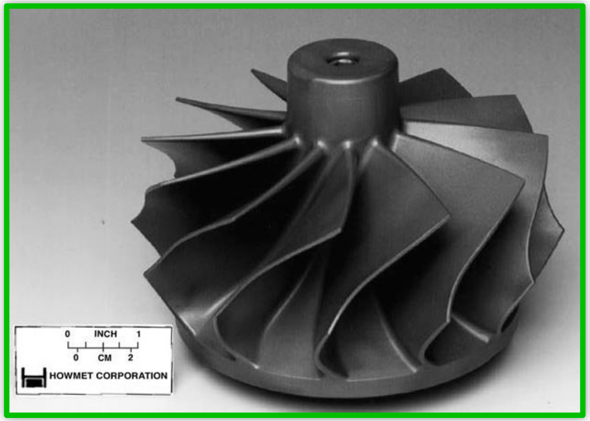
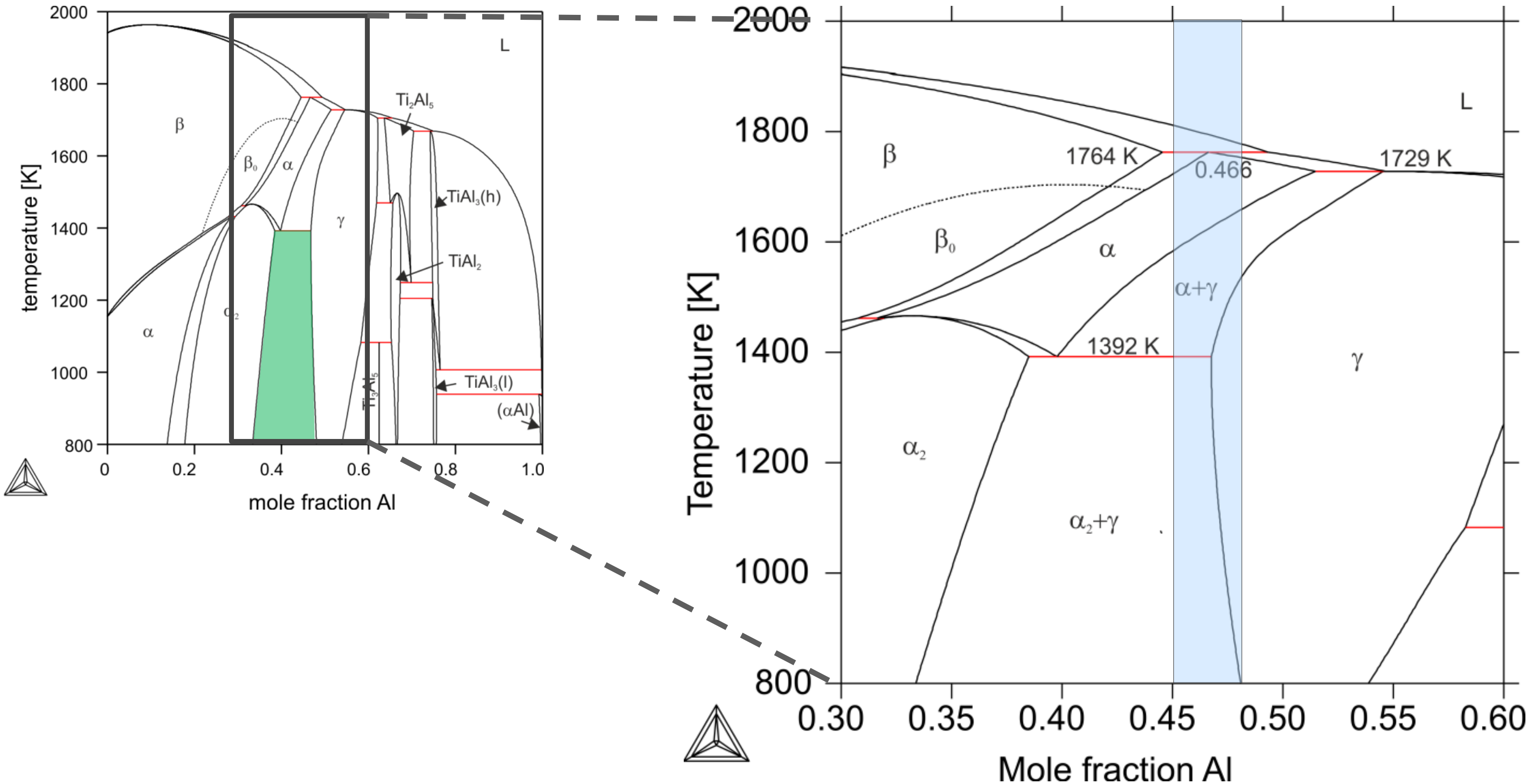
Alloy development for AM – TiAl

- Ti-Al alloys of interest for high temperature structural components
  - low density (~3.9-4.2 g/cm^3)
  - high Young's modulus (~140 GPa), high strength, creep resistant
  - higher oxidation resistance than Ti alloys
  - higher service T than Ti alloys
- Fully intermetallic
  - low elongation to fracture, brittle at room temperature
  - sensitive to contamination, properties strongly dependent on phase morphology
  - Extremely difficult to process by AM





The system Ti-Al



AM of a Ti-45Al-3Nb alloy

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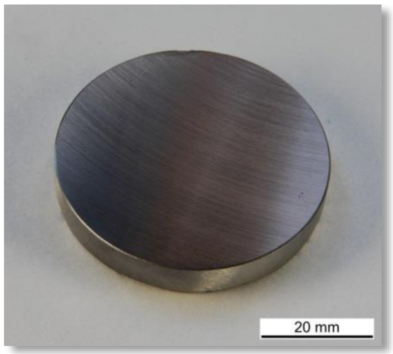
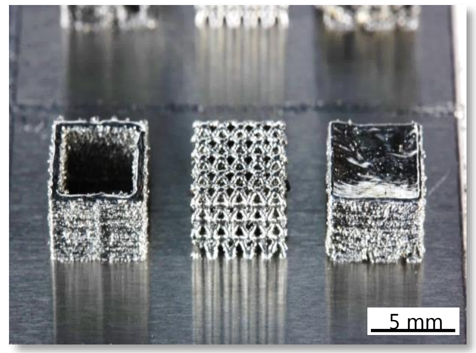
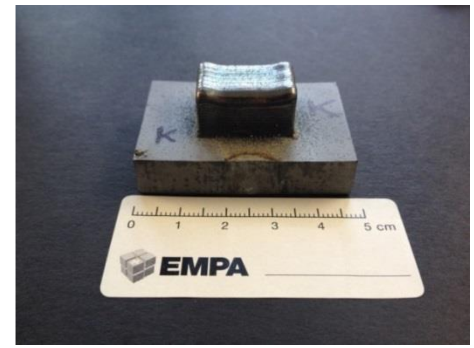
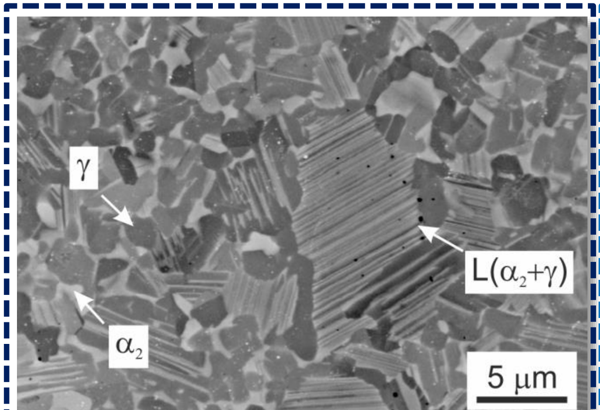
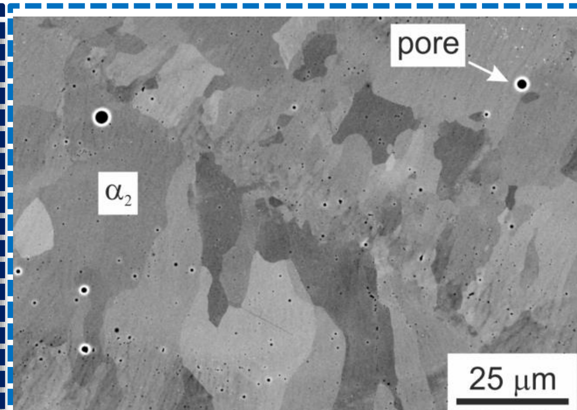
Sintering (SPS)	SLM	LMD

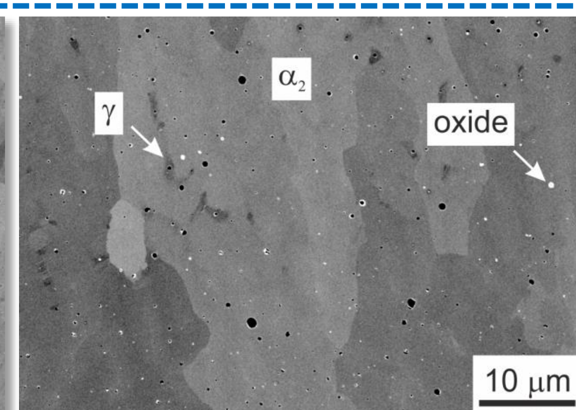






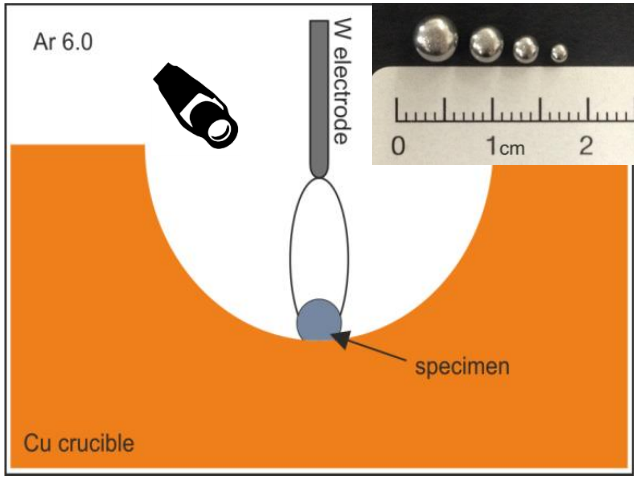


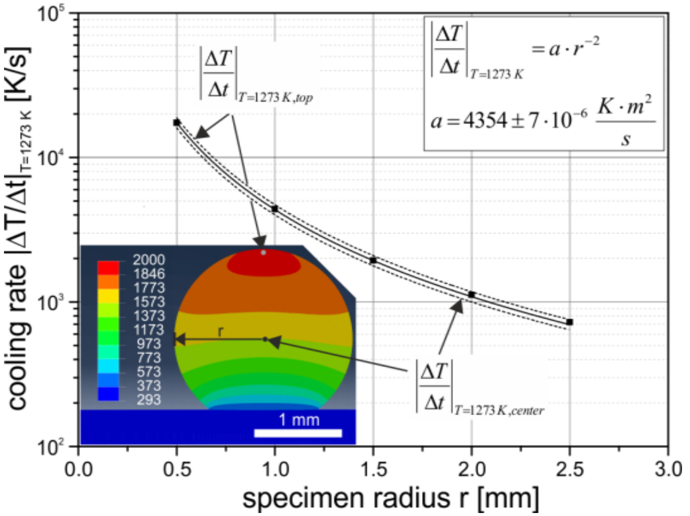




Kenel, C. *et al.*, 2016, in preparation

Rapid solidification – basic offline tests

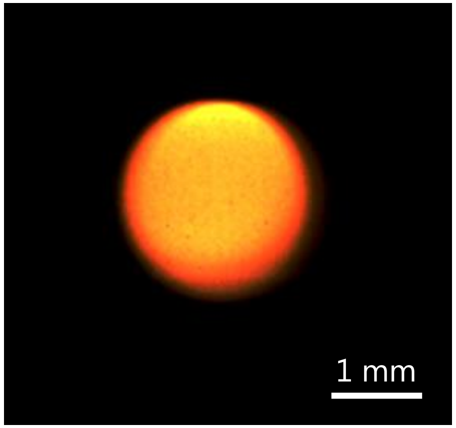


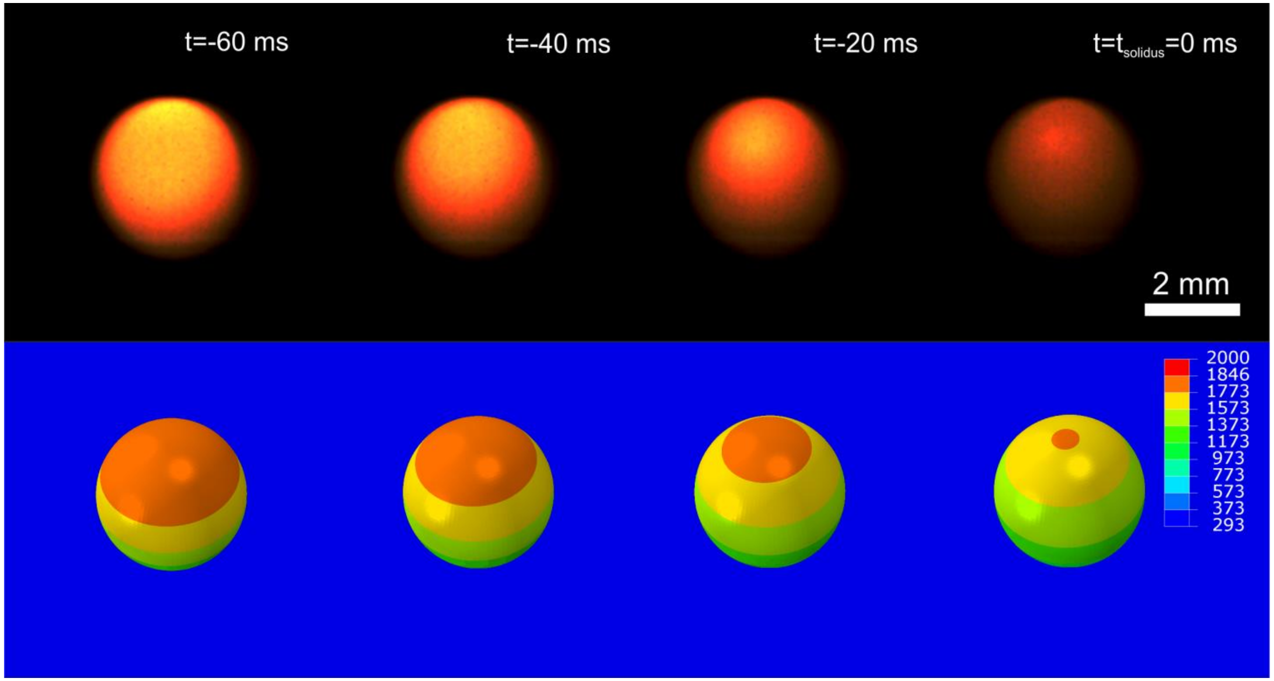


- heating and rapid solidification of small samples using W-electrode arc melting or laser beam melting
- size dependent cooling rates
  - spherical samples, the smaller the faster
  - cooling rate ~ r^{-2}
- function correlating radius and cooling rate
  - single «material» parameter to describe the complete curve
- simulation verification by high speed camera measurement
  - comparable solidus propagation in experiment and simulation

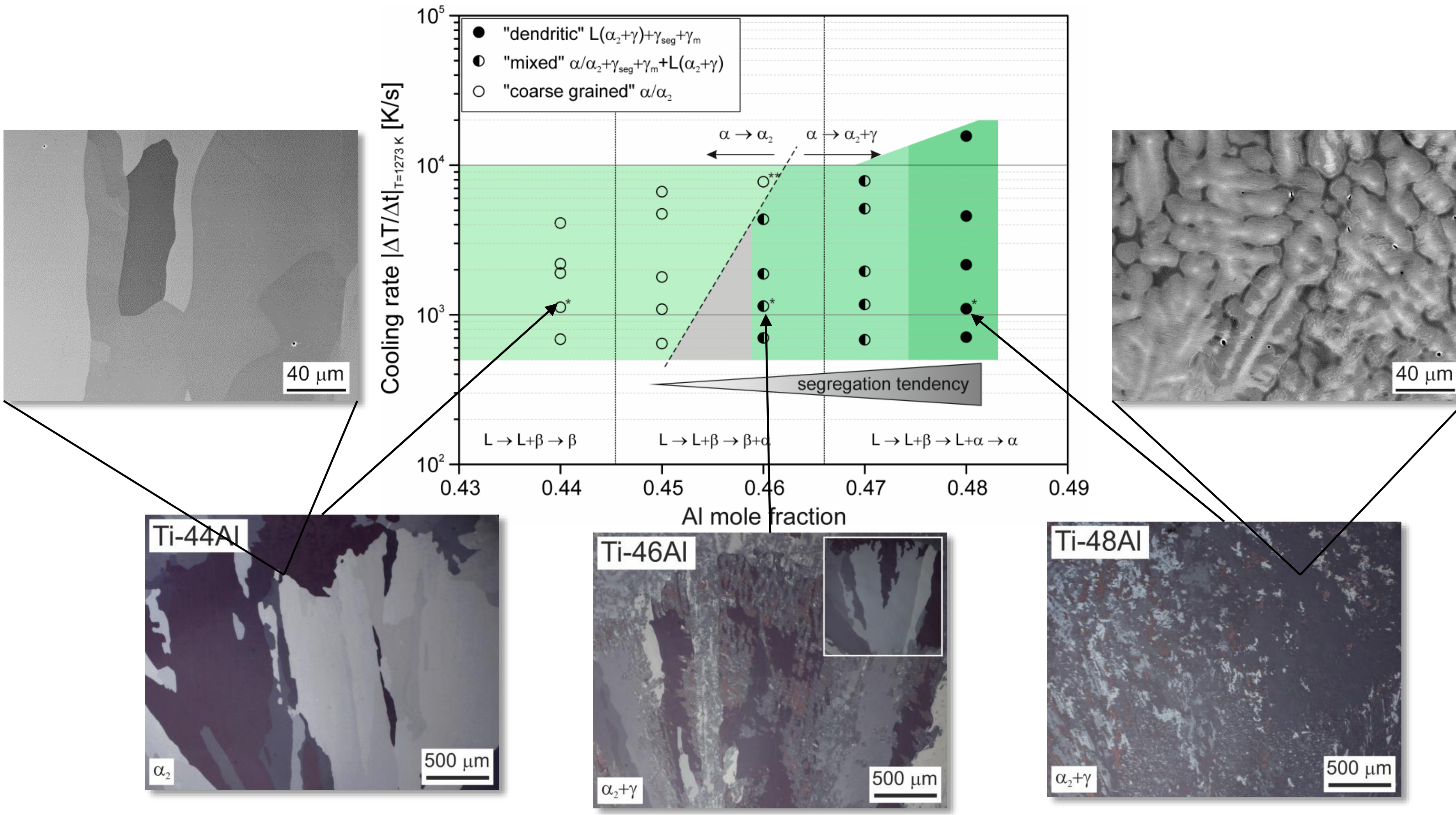
/Kenel C, Leinenbach C. J Alloys Compd 2015;637:242/

Comparison measurement - simulation





Influence of cooling rate on microstructure formation



Kenel C, Leinenbach C. J Alloys Compd 2015;637:242.

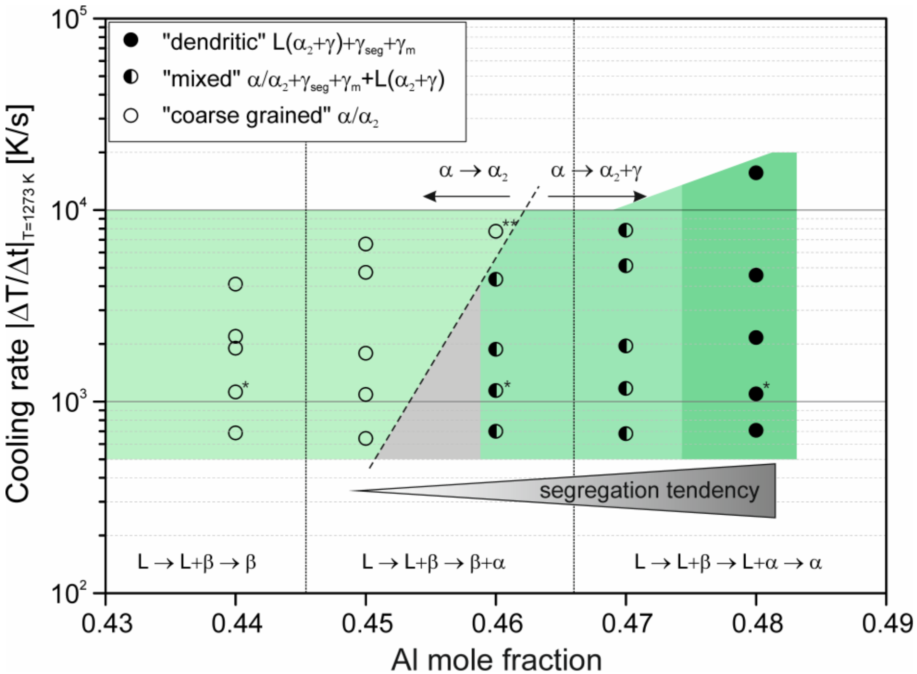
Influence of cooling rate on microstructure formation

$\alpha \rightarrow \alpha_2$ ordering

single phase

oversaturated α_2

extremely brittle



$\alpha \rightarrow \alpha_2 + \gamma$

out-of-process two phase

desired set of phases

tough

- composition – cooling rate – microstructure maps
  - properties relevant to processing (here: formation of intermetallic phases)
  - data for alloy selection
  - similar to processing window determination experiments → indications for suitable processing parameters
- predictability based on equilibrium phase diagram information: limited

Construction of phase selection hierarchy maps

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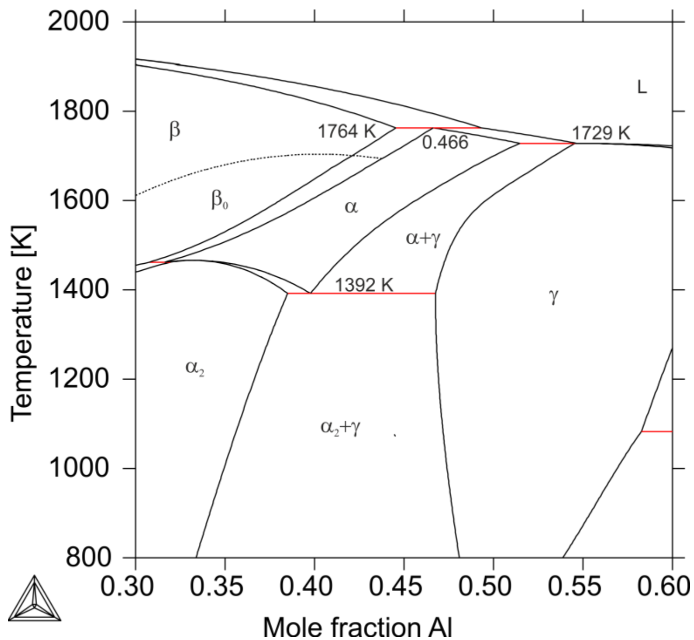
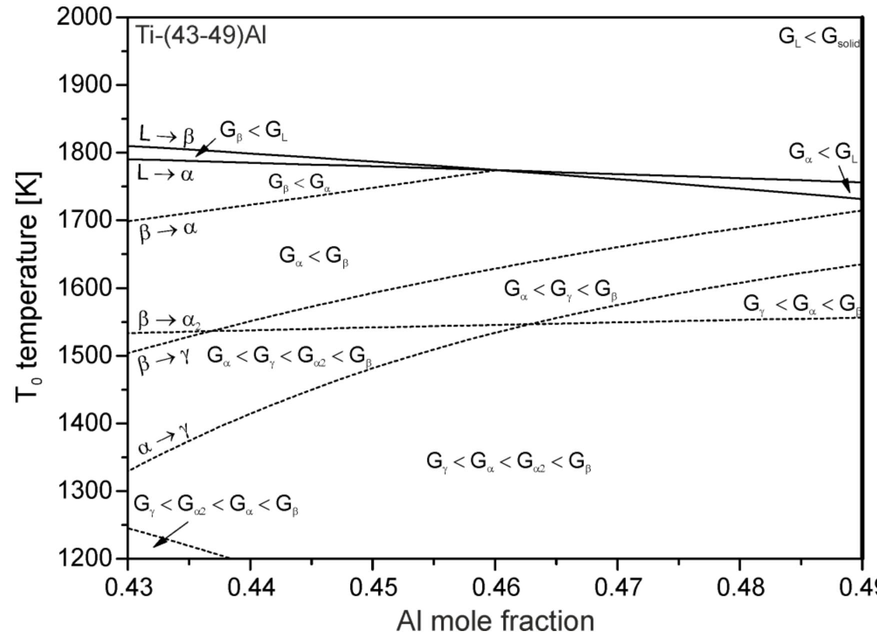
equilibrium



non-equilibrium



- T_0 temperatures for different phase transformations and solidification
  - calculated using CALPHAD
  - based on published thermodynamic assessment for Ti-Al [VT Witusiewicz et al. J Alloys Compd 2008;465:64]
- map constituents
  - T_0 temperature curves for specific phase transformations
  - fields with a hierarchy according to the Gibb's free energy
- «phase diagram without diffusion»

/C. Kenel, CL. J Alloys Compd 2015;637:242/

Construction of phase selection hierarchy maps

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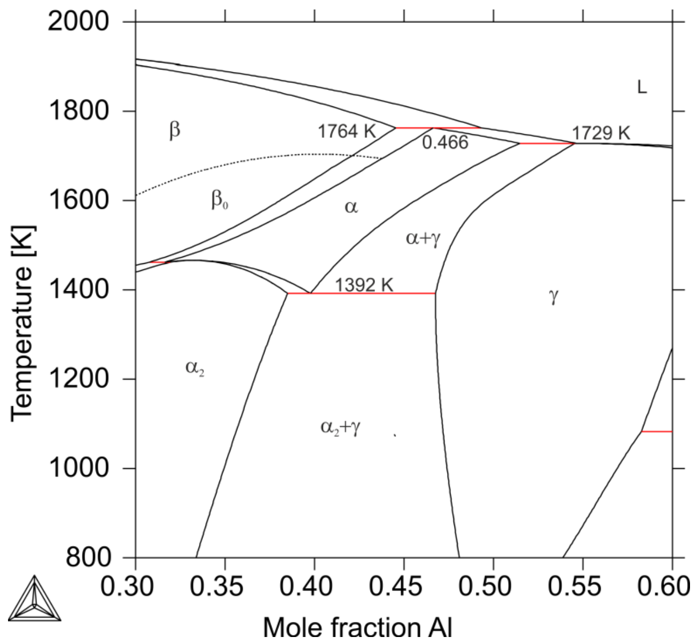
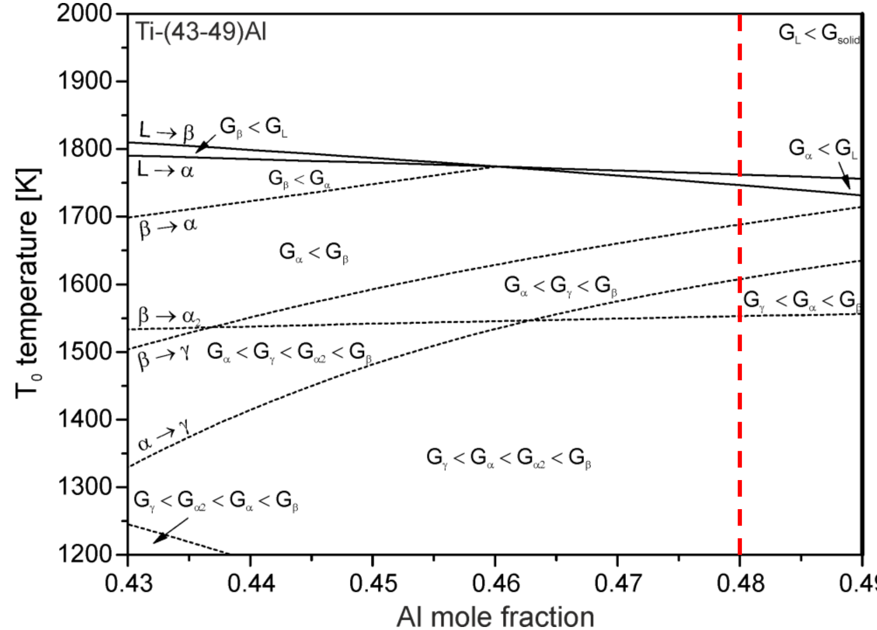
equilibrium



non-equilibrium



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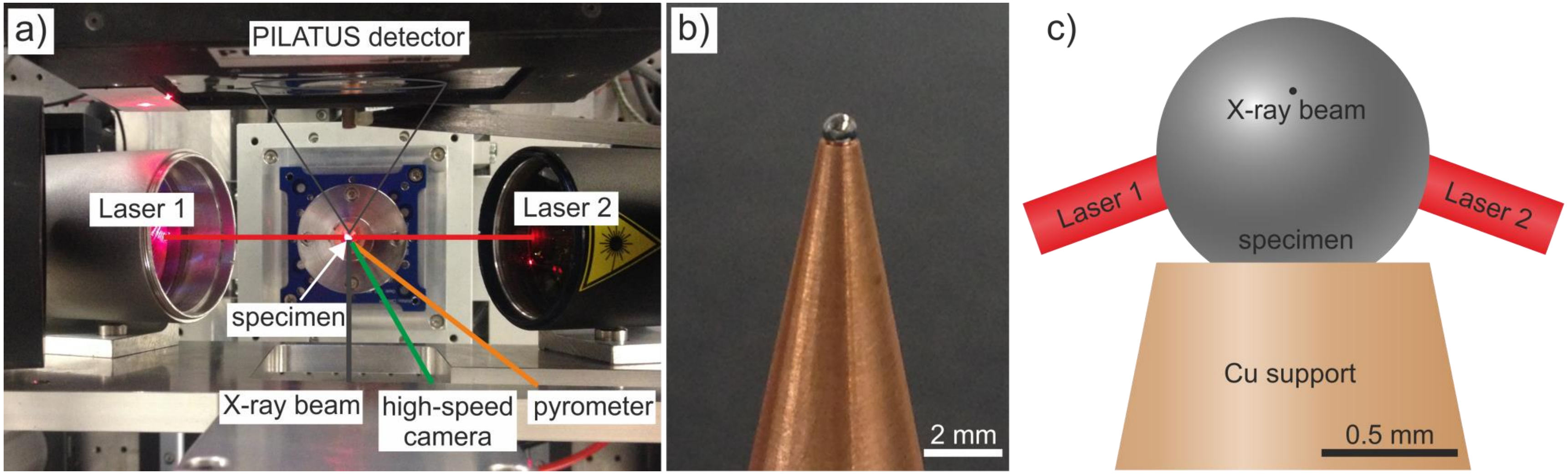
/C. Kenel, CL. J Alloys Compd 2015;637:242/

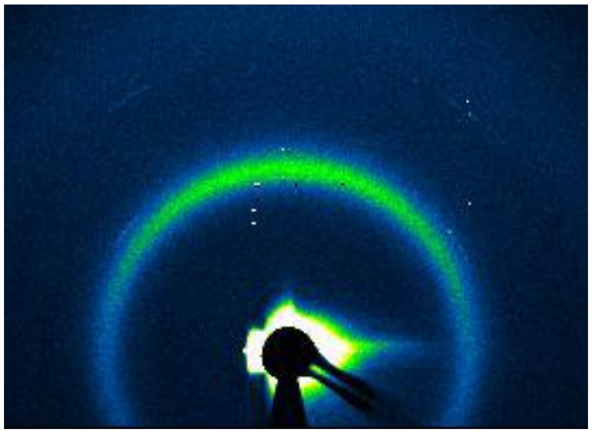
Validation - In situ microXRD tests



- Laser heating setup in microXAS beamline at Paul-Scherrer-Institut
- Rapid melting and solidification in spherical alloy specimens; cooling rate determined by sphere radius (C. Kenel, CL. J Alloys Compd 2015;637:242)
- Time resolved characterization of phase transformations during rapid solidification using microXRD (transmission) and high speed imaging
- Study of solidification sequence in Ti-48Al at cooling rate of $1.25 \cdot 10^3$ $K \cdot s^{-1}$

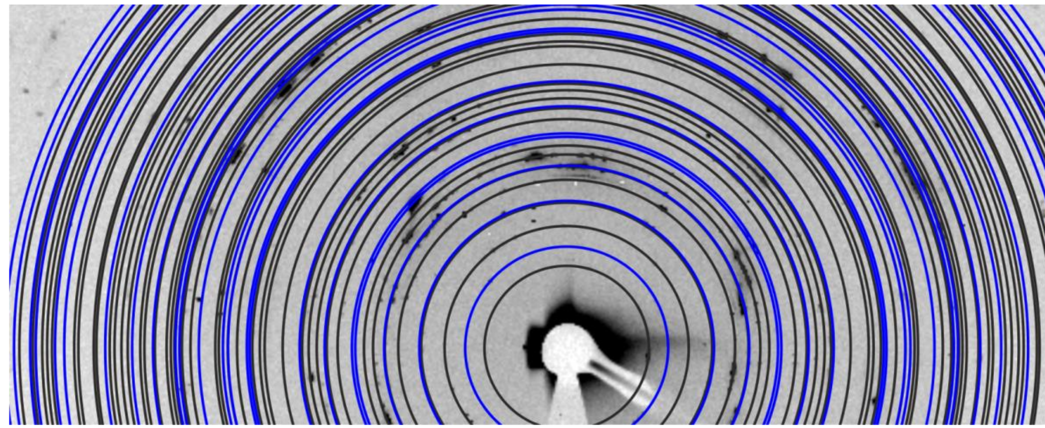
/C. Kenel, D. Grolimund, J.L. Fife, V.A. Samson, S. Van Petegem, H. Van Swygenhoven, CL, Scripta Mater 2016:114;117/

In situ microXRD tests



t_{tot} = 1.5 s

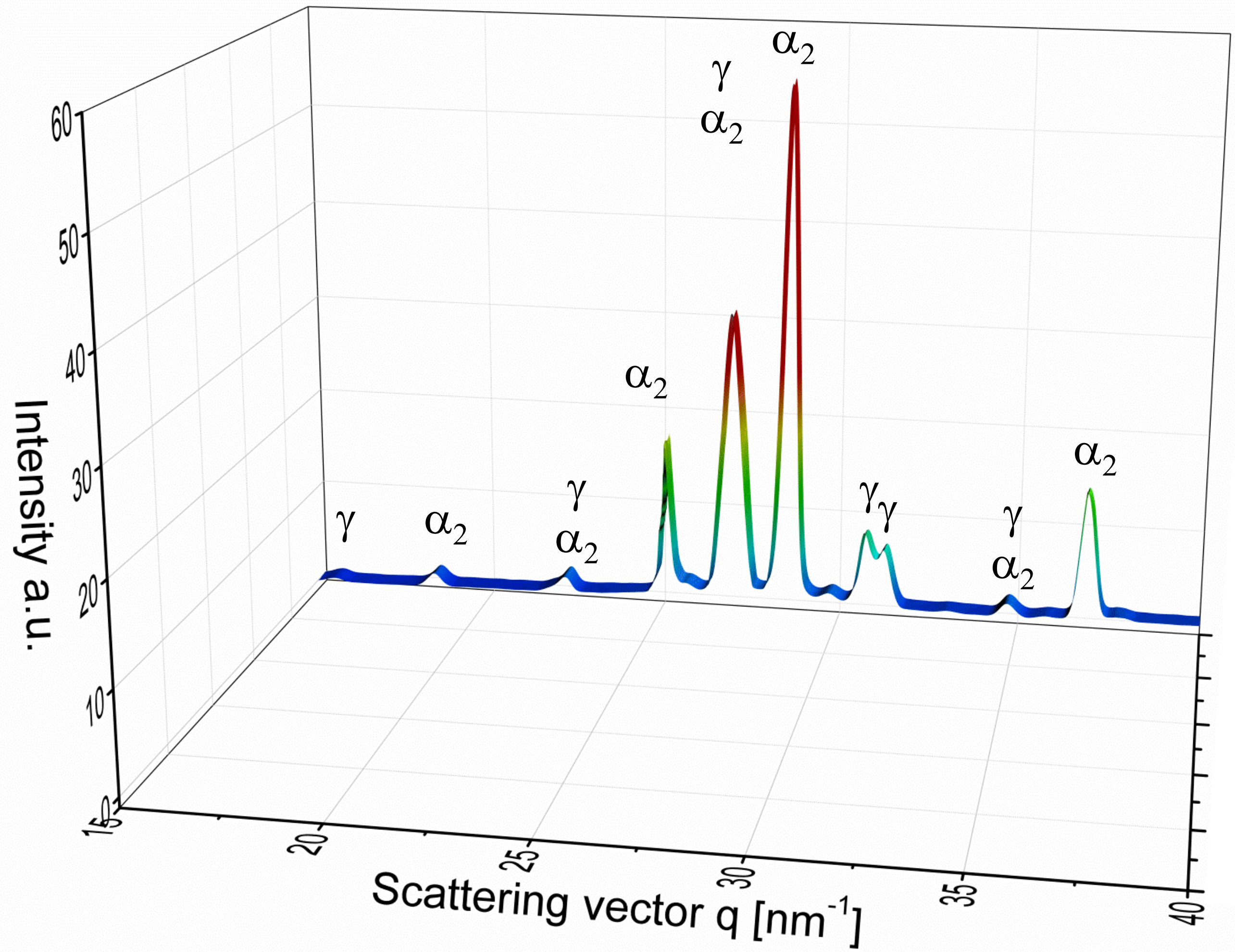
Ti_3Al **TiAl**



- Laser heating until stable melt is reached for >1s and shut-off
- Azimuthal integration for time evolution series
- 1 Experiment = 2000 2D spectra (new measurements: 10000 2D-spectra!)

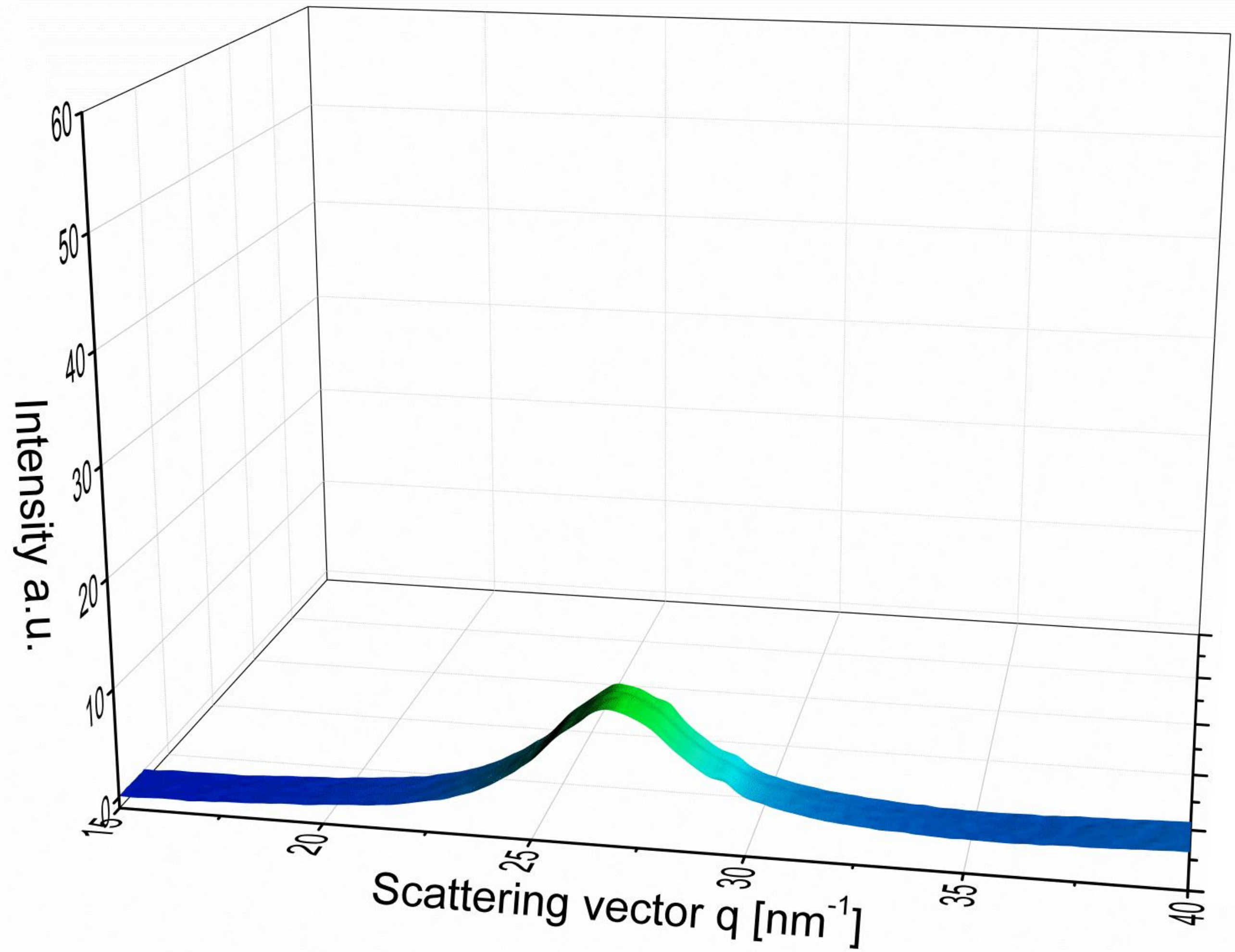
/C. Kenel, D. Grolimund, J.L. Fife, V.A. Samson, S. Van Petegem, H. Van Swygenhoven, CL, Scripta Mater 2016:114;117/

In situ microXRD on binary Ti-48Al



- Low T: Fully intermetallic dual phase structure

In situ microXRD on binary Ti-48Al



- Low T: Fully intermetallic dual phase structure
- High T (~1500°C): metallic liquid

In situ microXRD on binary Ti-48Al

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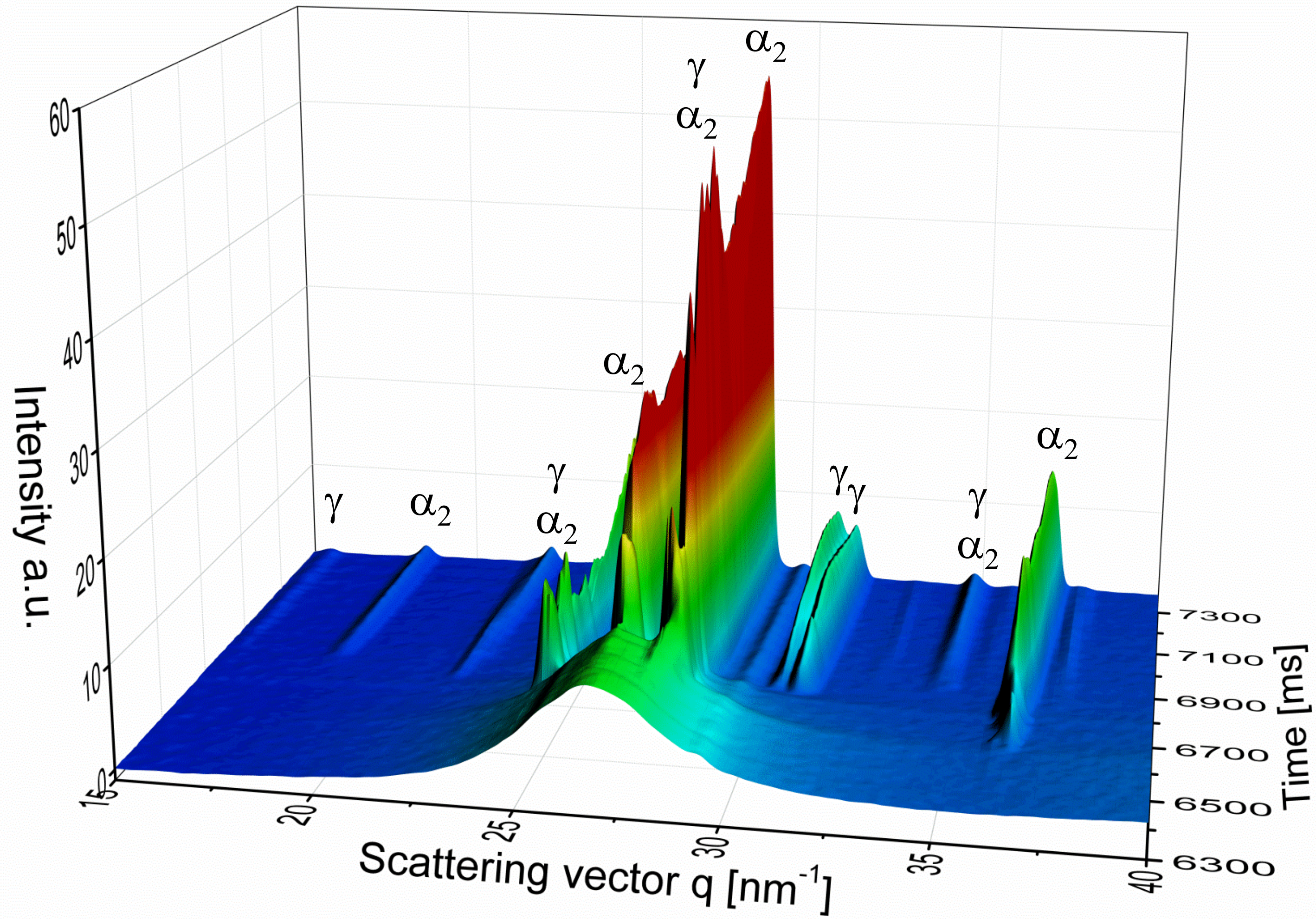
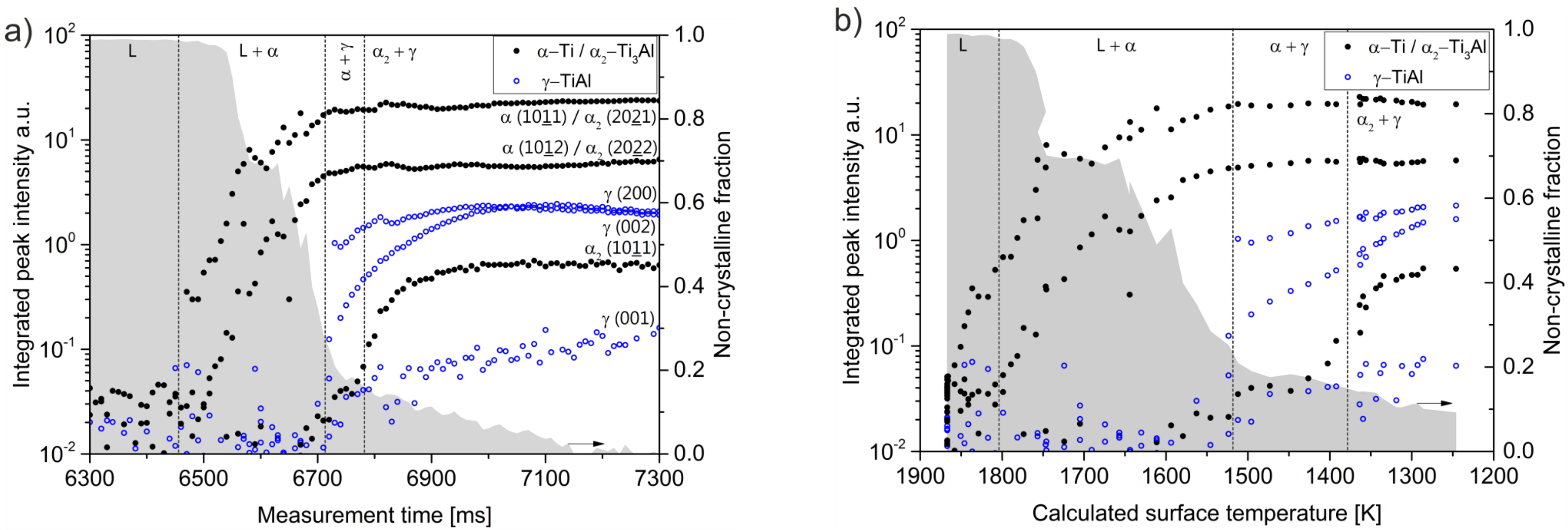


- Low T: Fully intermetallic dual phase structure
- High T (~1500°C): metallic liquid
- and everything in between....

In situ microXRD tests



- Analysis of peak evolution and non-crystalline fraction shows the coexistence of the liquid phase and the α-phase upon solidification
- Pixel intensities on CCD chip can be correlated with actual surface temperature

$$I_{CCD} = \frac{a \cdot c_{1L}}{\exp\left(\frac{c_2}{b \cdot T}\right) - 1}$$

- Based on the presented results, the non-equilibrium solidification and transformation of Ti-48Al follows: L→L+α→ α+γ_{seg}→ α+γ+ γ_{seg}→ α_2+ γ

/C. Kenel, D. Grolimund, J.L. Fife, V.A. Samson, S. Van Petegem, H. Van Swygenhoven, CL, Scripta Mater 2016:114;117/

Phase evolution under AM conditions

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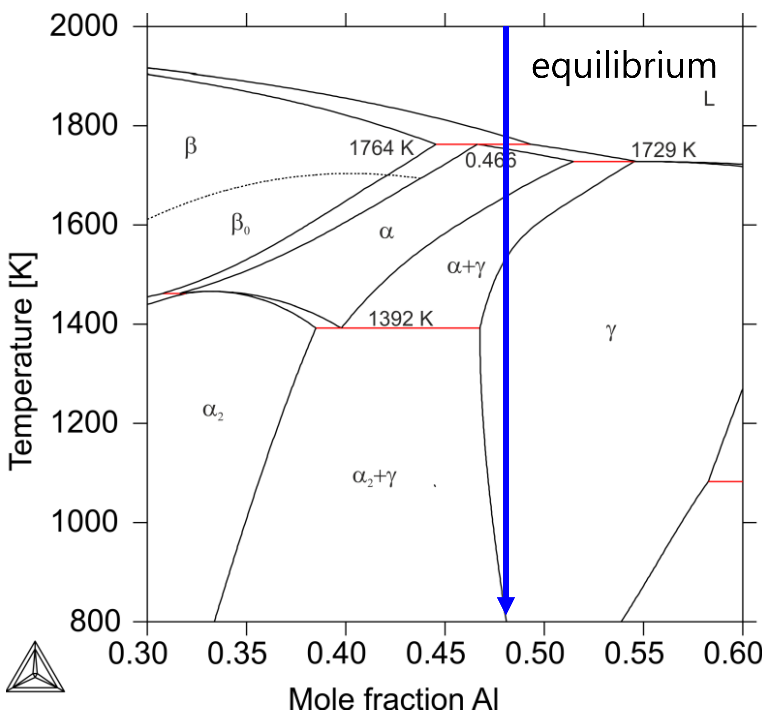
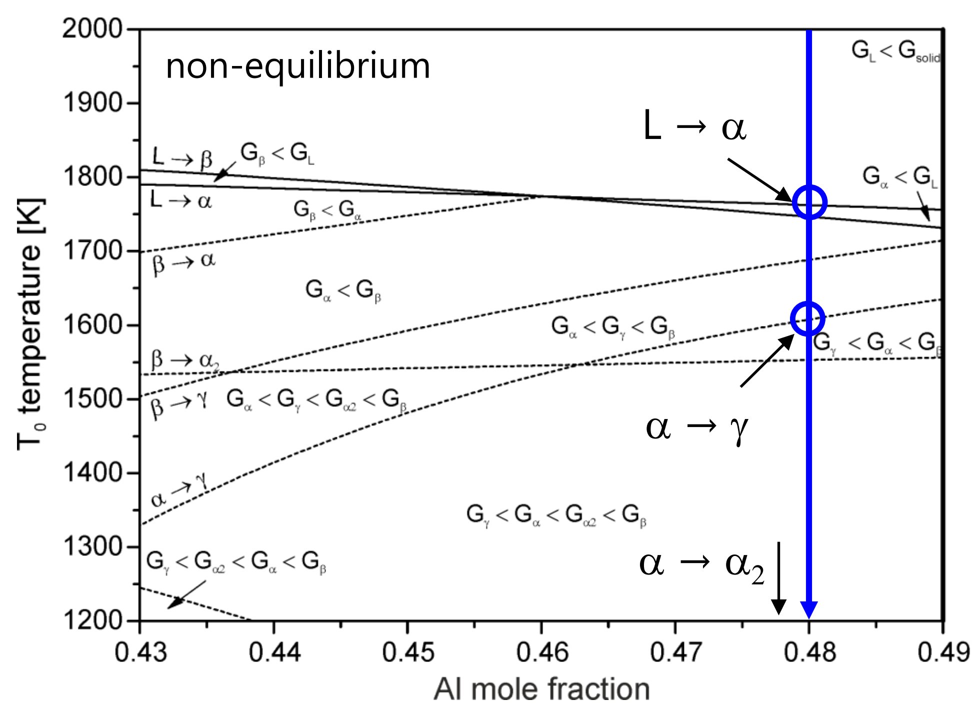
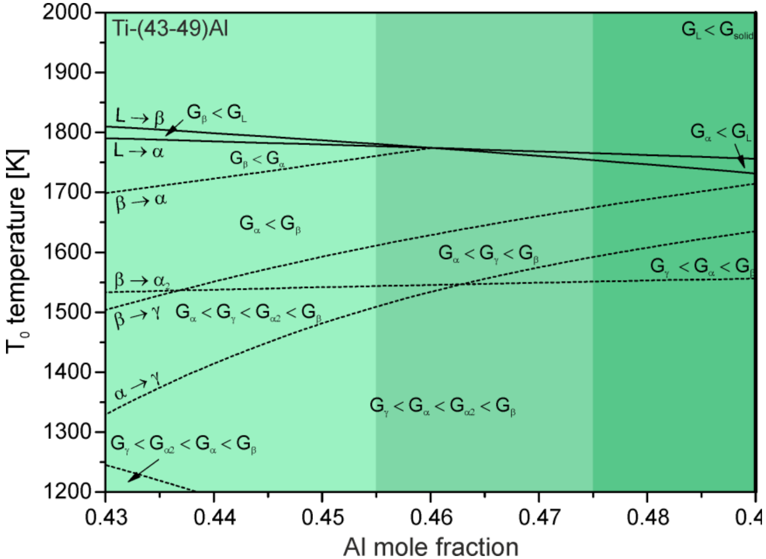
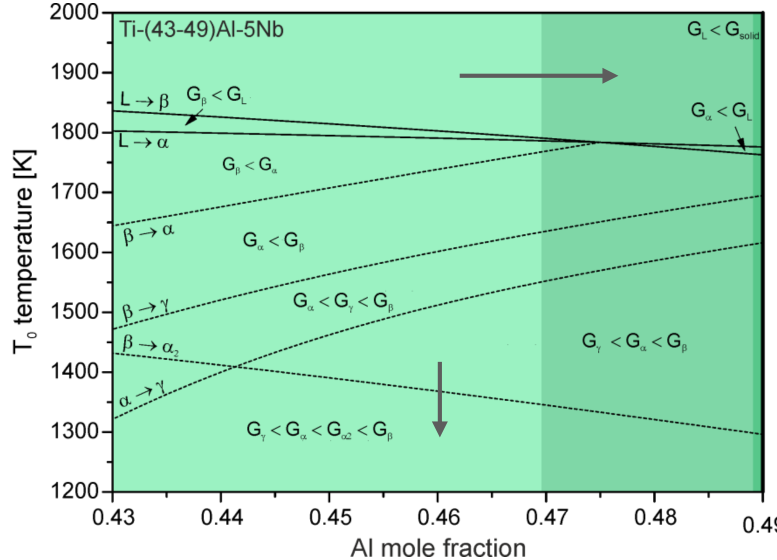




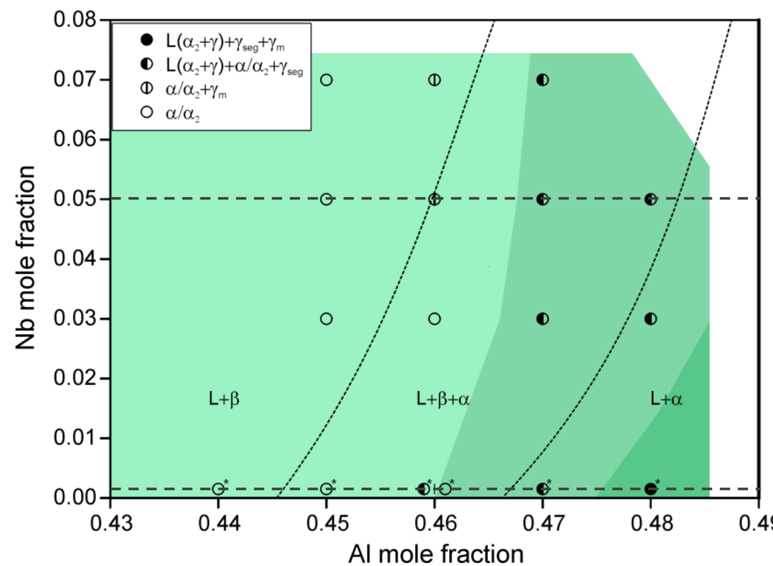
- Phase transformation sequence
  - Full equilibrium: $L \rightarrow L + \beta \rightarrow L + \beta + \alpha \rightarrow L + \alpha \rightarrow \alpha \rightarrow \alpha + \gamma \rightarrow \gamma \rightarrow \gamma + \alpha_2$
  - AM conditions: $L \rightarrow L + \alpha \rightarrow \alpha \rightarrow \alpha + \gamma \rightarrow \gamma + \alpha_2$
    - Preference of α over β under non-equilibrium conditions
    - Early formation of γ
    - Suppression of full $\alpha \rightarrow \gamma$ transformation and direct ordering $\alpha \rightarrow \alpha_2$

Influence of Nb on microstructure



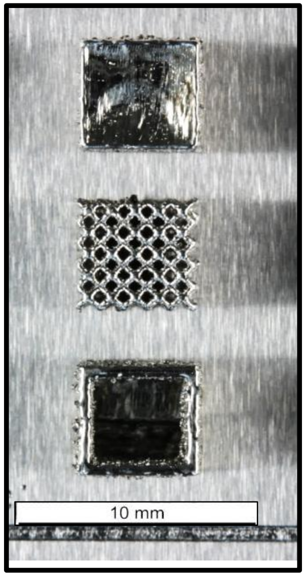


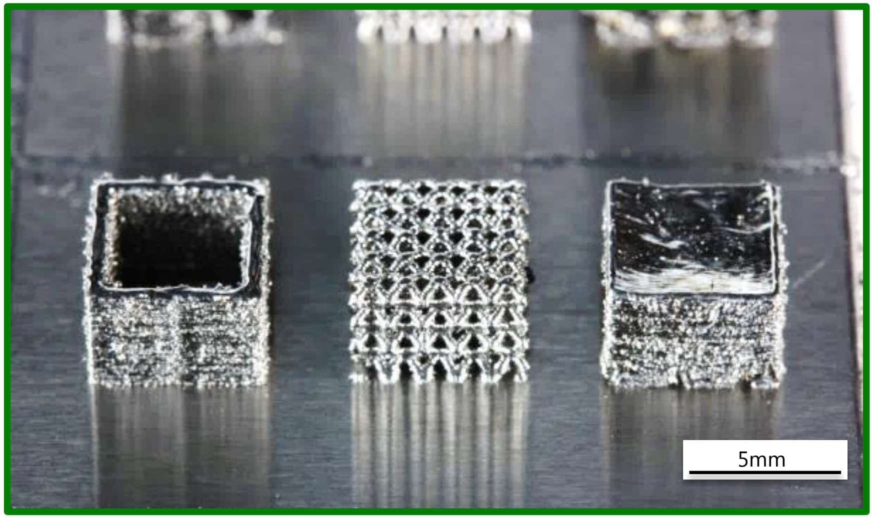
- Calculations in good agreement with experimental data
- T_0 concept allows to predict
  - changed transformation behavior
  - non-equilibrium effects
  - changed transformation tendencies
- if the thermodynamic assessments are available and are of sufficient quality

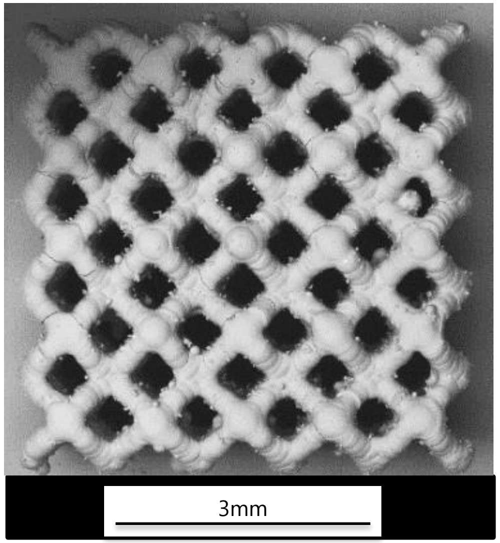


/C. Kenel, CL, Intermetallics 2016;69:82/

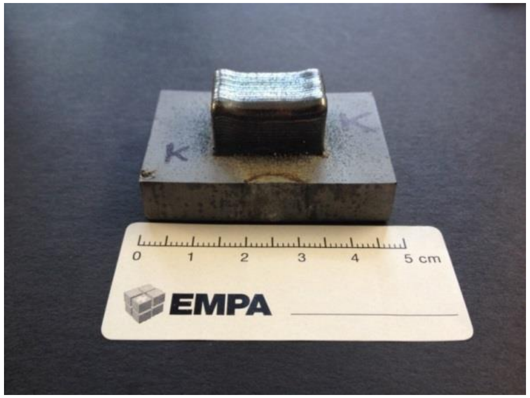
AM of TiAl with more complex geometries



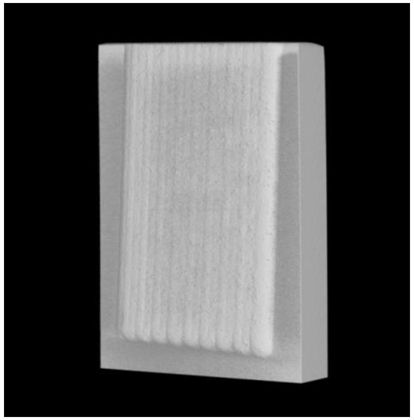




SLM 3D test structures (in collaboration with Inspire)



LMD test structure Ti-Al alloy (with TWI Ltd.)



CT of a LMD test specimen

in collaboration with

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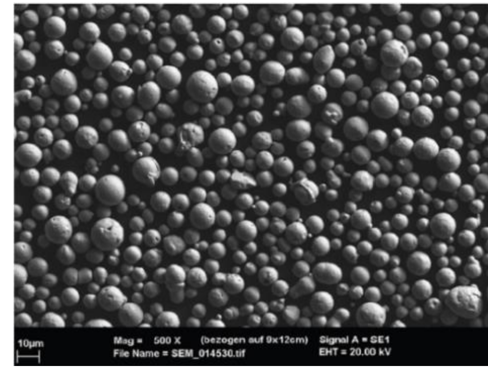
New materials by AM
Metal-diamond composites

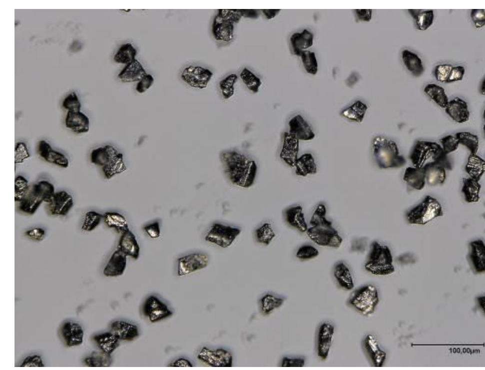
- Metal-diamond composites interesting for high-performance cutting or grinding tools
- Conventional production: Galvanic Ni-bonding of diamond particles
  - Only single layer diamond tools possible, typically with simple geometry
- AM offers possibility to produce complexely shape geometries (e.g. internal cooling chanels
- Problem: Graphitization tendency of diamond particles at elevated temperatures
  - Depending on atmosphere (Inert atmosphere / vacuum ≈ 1’500° , Air ≈ 1’000°C)

Metal-diamond composites

- Matrix material
  - Cu-14Sn-10Ti alloy
  - High thermal conductivity (> ≈ 55 W/mK)
  - $T_{liquidus}$ = 925°C
  - Powder with
    - D_{10} = 7.6µm
    - D_{50} = 20µm
    - D_{90} = 38µm



- Diamond particles
  - 50 vol% Ni-coated to protect the diamond particles from graphitization (additional heat sink)
  - Mean particle ∅ 33.9 ± 6.4µm



Metal-diamond composites

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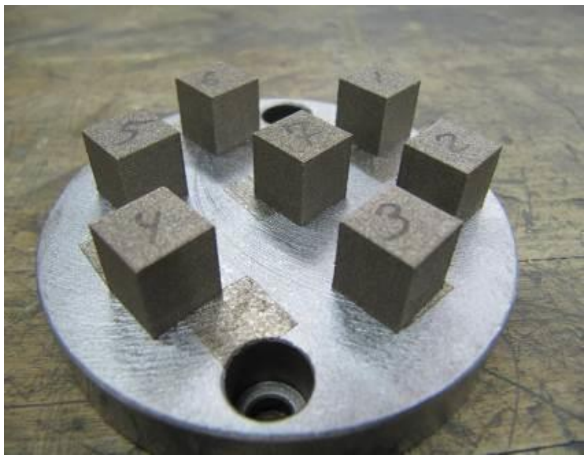
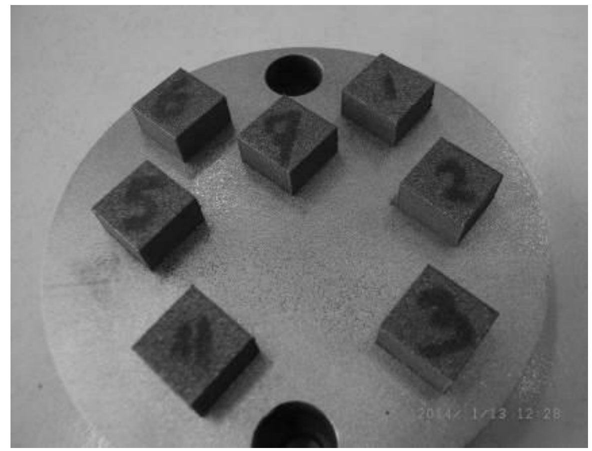
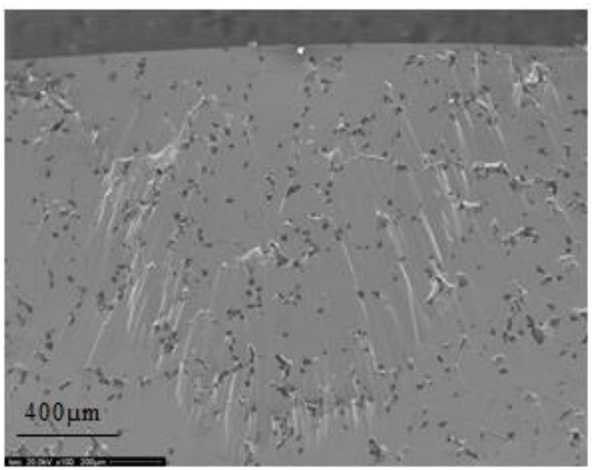
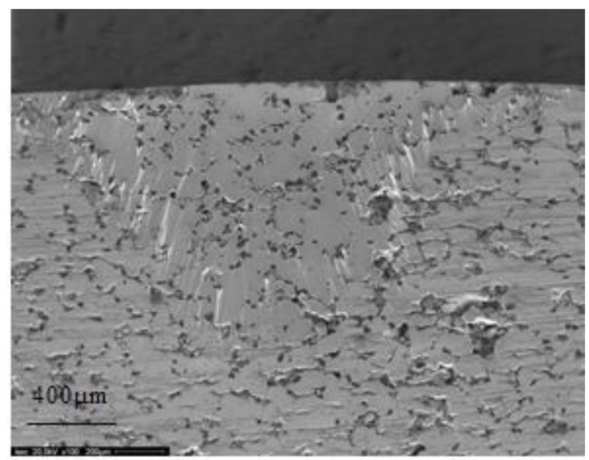
- SLM processing of a of Cu-Sn-Ti alloy & diamond particles
  - Stable specimens with good surface quality can be produced







Diabraze with 10 vol% Ni-coated diamond, EL = 50.5 $^{J}/_{mm^3}$



Diabraze with 20 vol% Ni-coated diamond, EL = 41.2 $^{J}/_{mm^3}$

/A.B. Spierings, CL, C. Kenel. K. Wegener, Rapid Prot J, 2016; 21(2):130-136/

Metal-diamond composites

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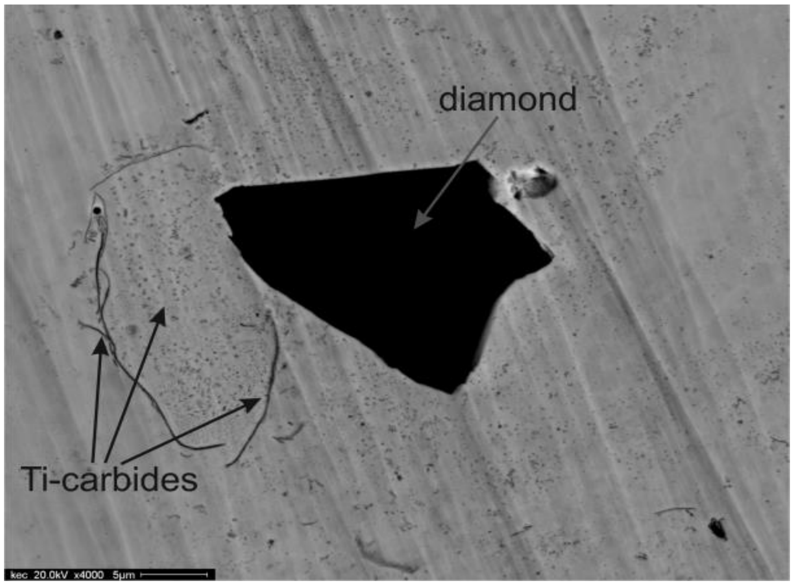
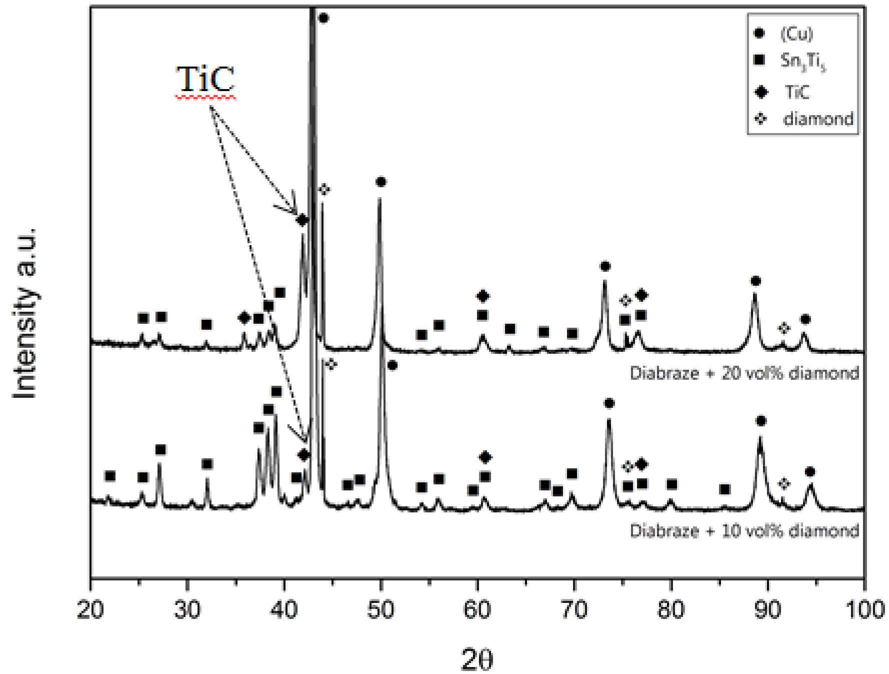
Integrity of diamonds after SLM



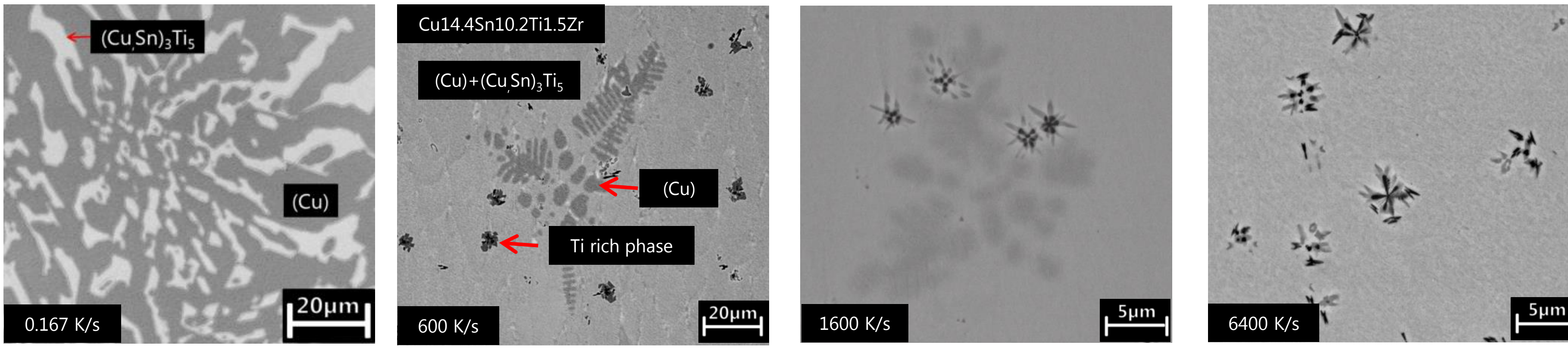


/A.B. Spierings, CL, C. Kenel. K. Wegener, Rapid Prot J, 2016; 21(2):130-136/

- Intact diamonds, embedded in the matrix
- Diamonds are surrounded by very small TiC particles

→ Diamond particles partly dissolves into the matrix during the SLM-process, forming TiC particles

Cooling rate dependent microstructure in Cu-Sn-Ti alloys

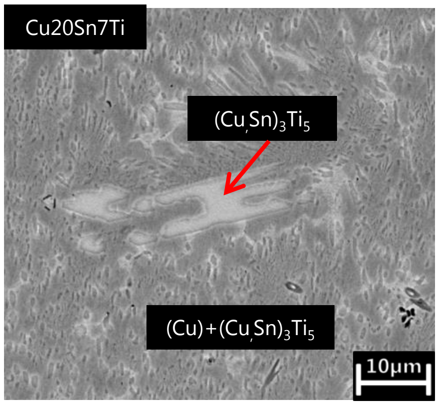


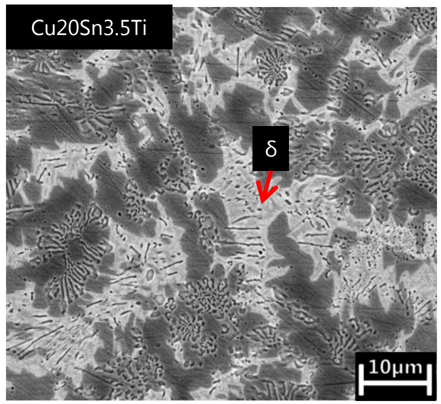
in wt.%

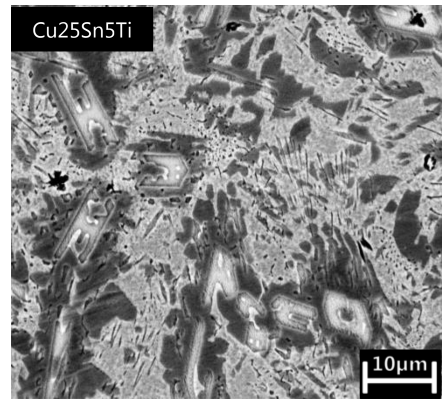
- Main phase constitutes (fcc (Cu) and $(Cu,Sn)_3Ti_5$) don’t change with modification of cooling rate.
- Increasing cooling rate:
  - Grain sizes significantly decrease
  - Morphorlogy: eutectic lamelar structures
  - Suppress of densritic primary phase
  - Small amount of Ti enriched phases

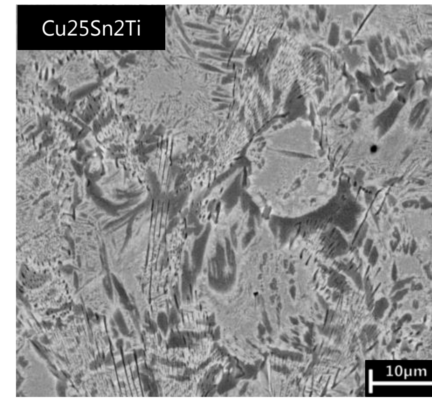
Composition dependent microstructure in Cu-Sn-Ti alloys

cooling rate ~600 K/s









- Slightly changing the Ti content, the amount of large IMC is reduced.
- Different Sn/Ti ratios:
  - The phase constitutes change, i.e. new δ phase
  - The morphology of (Cu) phase varies from dendrite to non-dendritic shape.

- Materials aspects related to AM – some basics
- Development of an ODS-TiAl alloy for AM
  - Microstructure formation during rapid solidification
  - Microstructure of AM processed ODS-TiAl
- Development of bronze/diamond composites for AM
  - SLM processing of bronze/diamond composites
  - Rapid solidification of Cu-Sn-Ti alloys
- Summary and outlook

Summary

- Metal additive manufacturing offers novel and hitherto unknown possibilities in terms of geometry and functionality of components
- To exploit those possibilities, the understandig and optimization of the currently existing alloys or the development of novel alloys is necessary
- It is crucial to know the phase relations in the alloys of interest as well as the phase transformation behaviour under the rapid solidification conditions during laser AM
- ...we are only at the beginning. Real additive MANUFACTURING (not prototyping) requires a better understanding of the correlation between design, materials, manufacturing process and component properties

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...the people at Empa

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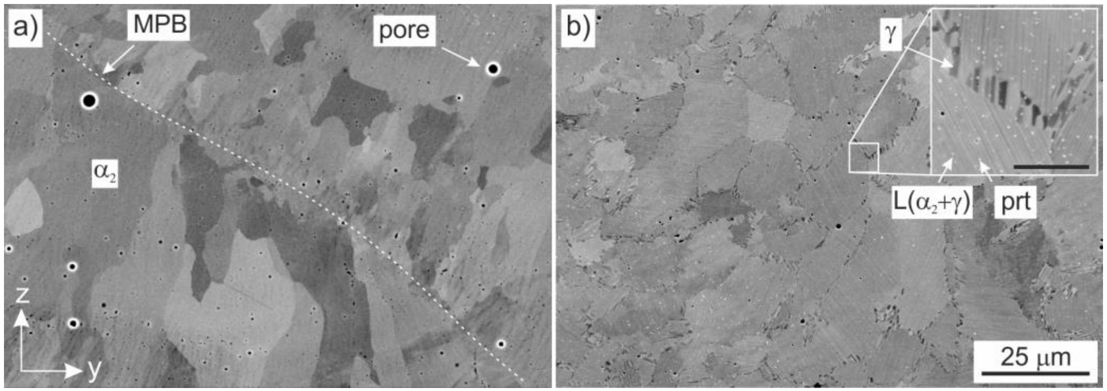
- Valerie Ann Samson, PSI
- Julie L. Fife, PSI
- Steven van Petegem, PSI
- Helena van Swygenhofen, PSI

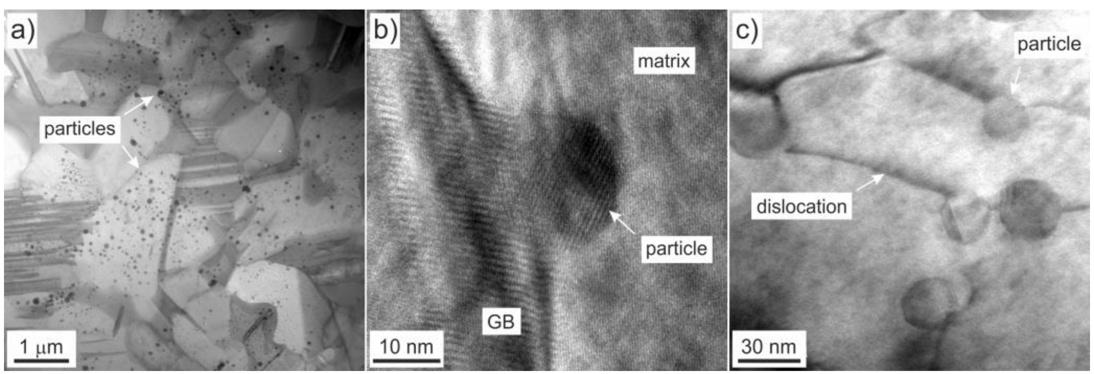
Microstructure of AM ODS-TiAl

SEM



a) as processed state → meta-stable microstructure
b) after thermal annealing at 1123 K for 12 h (inset: scale bar = 4 mm) → ultra fine lamellar two-phase ($\alpha 2/\gamma$) microstructure.

TEM



a) STEM bright-field, distribution of fine ODS particles,
b) HRTEM micrograph of an ODS particle pinning a grain boundary (GB) in the intermetallic matrix
c) TEM micrograph of ODS particles interacting with dislocations.

Influence of AM process on oxide particles

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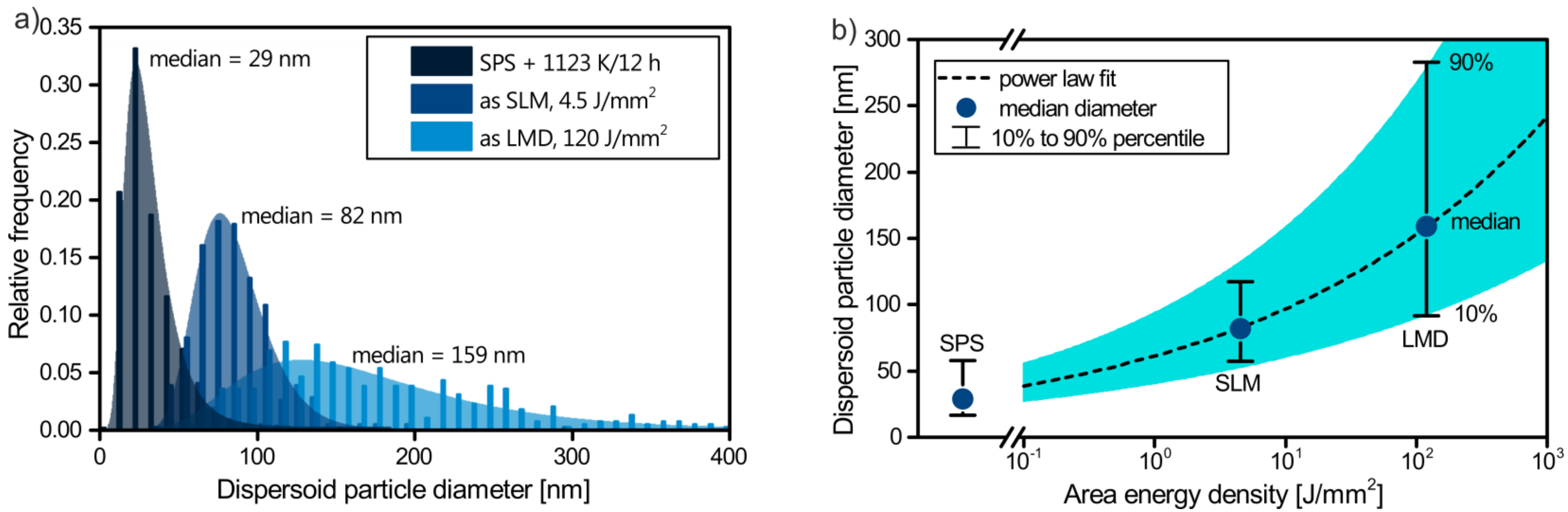

- AM processing leads to a certain degree of particle coarsening due to the high temperature and presence of a liquid phase
- Rapid growth can occur in the liquid state by incorporation of Ti and/or Al into oxides
- Reducing the energy input in the material during processing clearly reduces the preserved oxide particle size.

Properties of ODS-TiAl

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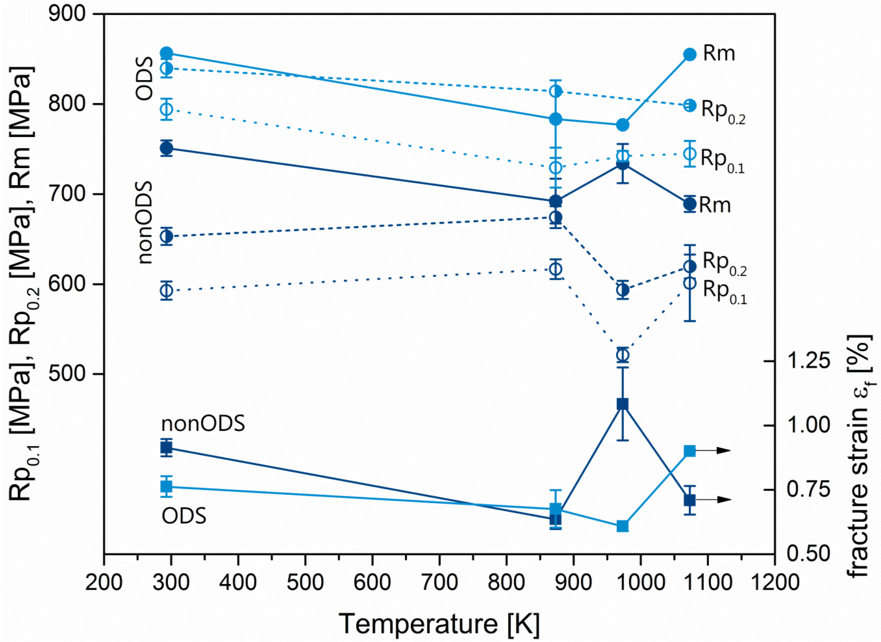
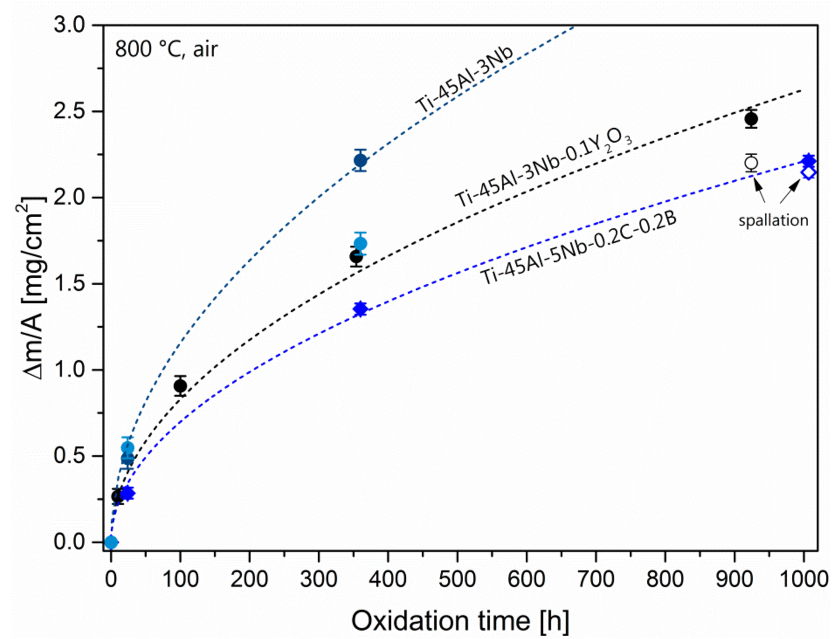
High temperature strength

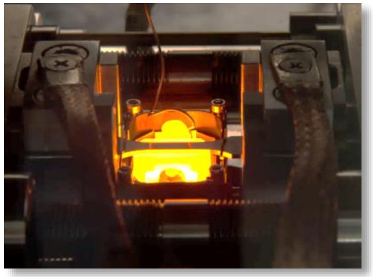


Oxidation behavior



ODS variant has

- Higher yield point
- Higher ultimate strength
- Lower ductility



Case 2: Ti-6Al-4V

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Full length article

Massive transformation in Ti–6Al–4V additively manufactured by selective electron beam melting

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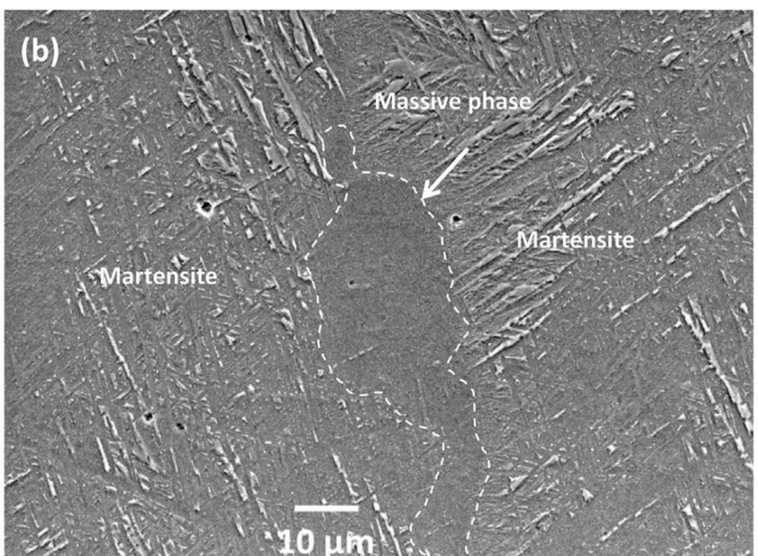
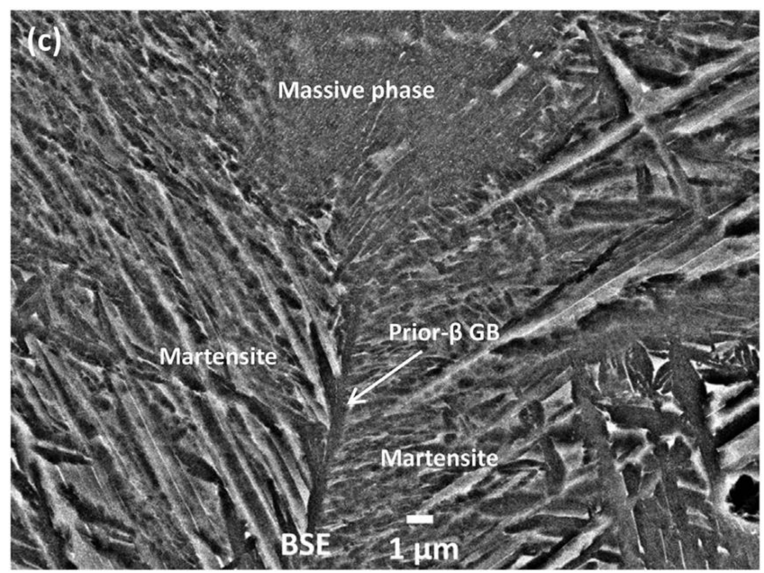
- EBM processed Ti-6Al-4V
- Observation of (unusual) massive hcp-α grains along former bcc-β grains in α′ (martensite) matrix
- Rack et al. showed that the massive transformation occurred in mill-annealed Ti-6Al-4V when cooled at cooling rates (defined at 900 C) between 20 K/s and 410 K/s.





Case 2: Ti-6Al-4V

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- Calculation of the Gibbs free energies of the hcp-α, bcc-β and liquidus phase based on the TTTi3 database
- The β → α+β transus temperature is known to be 970°C
- The M_s of Ti-6Al-4V is known to be ≈800°C
- The T_0-Temperature between hcp-α and bcc-β is calculated to 893°C

➢ the cooling rates during EBM are high enough that massive α grains can form in a diffusionless transformation between 893°C and 800°C

➢ the massive α grains are not stable and decompose into α+β lamellae as a result of the repeated re-heating during AM