Applications of CALPHAD based tools to additive manufacturing

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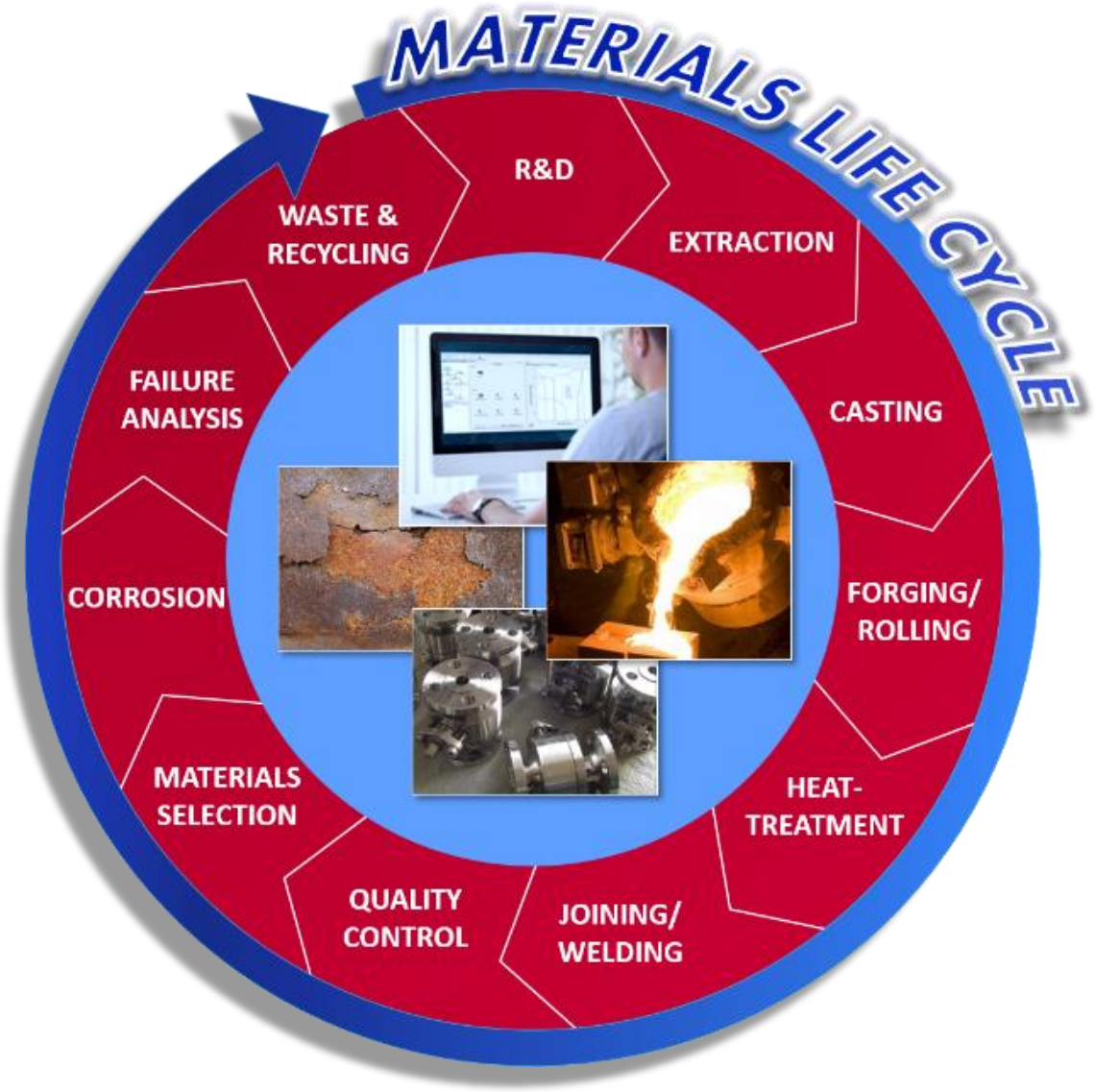
Derby, February 13, 2019

Thermo-Calc Software

- Company dedicated to provide computational tools in the field of materials engineering
- Founded in 1997
- Headquarters in Stockholm
- Offices in Pittsburgh, Zurich and Gothenburg
- Worldwide representation through local partners in e.g. Japan, China, India, South Korea, Russia, Australia, Brazil and Turkey
- > 1250 customers in 70+ countries

Applicability



By Application
Additive Manufacturing
Alloy development
Metallurgical extraction
Casting
Forging/Rolling
Heat-treatment
Joining/Welding
Quality Control
Materials selection
Corrosion
Failure analysis
Waste and re-cycling

By Material
Aluminium-based
Copper-based
Iron-based and steels
Magnesium-based
Nickel-based
Silicon-based alloys
Titanium-based
High Entropy alloys
Noble Metal alloys
Solder alloys
Other

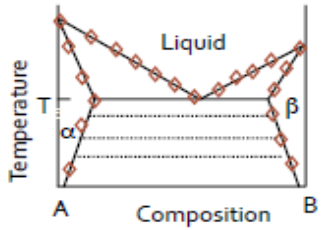
Outline

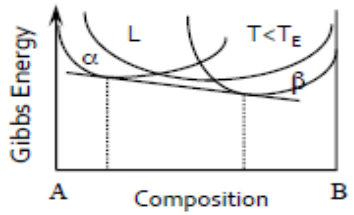
- Background on CALPHAD tools
- Materials challenges with additive manufacturing
- Applications to mechanical/thermal FEA modeling
- Applications to metallurgical phenomena
  - Alloy 625 Case study
    - Stress relief heat treatment promotes delta phase
  - 17-4 PH Case study
    - Predicting solidification behavior
    - Subsequent heat treatment
  - Ti-6Al-4V Case study
    - Predicting phase balance & microstructure morphology
  - Cracking Prediction Methods
    - Solidification, Liquation, Solid State
- Conclusion / Future Directions

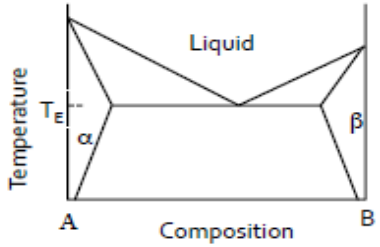
CALPHAD

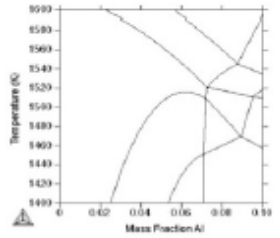
From C. E. Campbell, NIST

Experimental phase diagram and thermochemical data → Determine Gibbs energy functions for each phase: $G = f(x,T,P)$ → Calculated phase diagram → Combine binaries and ternaries to predict multi-component systems







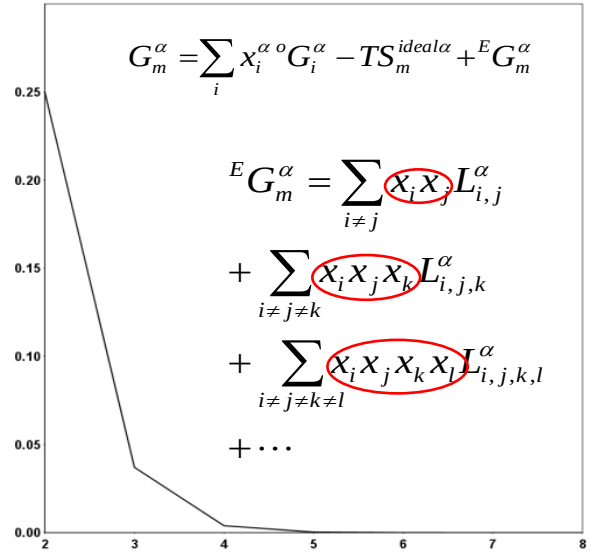


Al isopleth for 8 component system

$$G_m^{\alpha} = \sum_i x_i^{\alpha}\, {}^{o}G_i^{\alpha} - TS_m^{ideal\alpha} + {}^{E}G_m^{\alpha}$$

$$\prod_{i=2}^{n} x_i$$

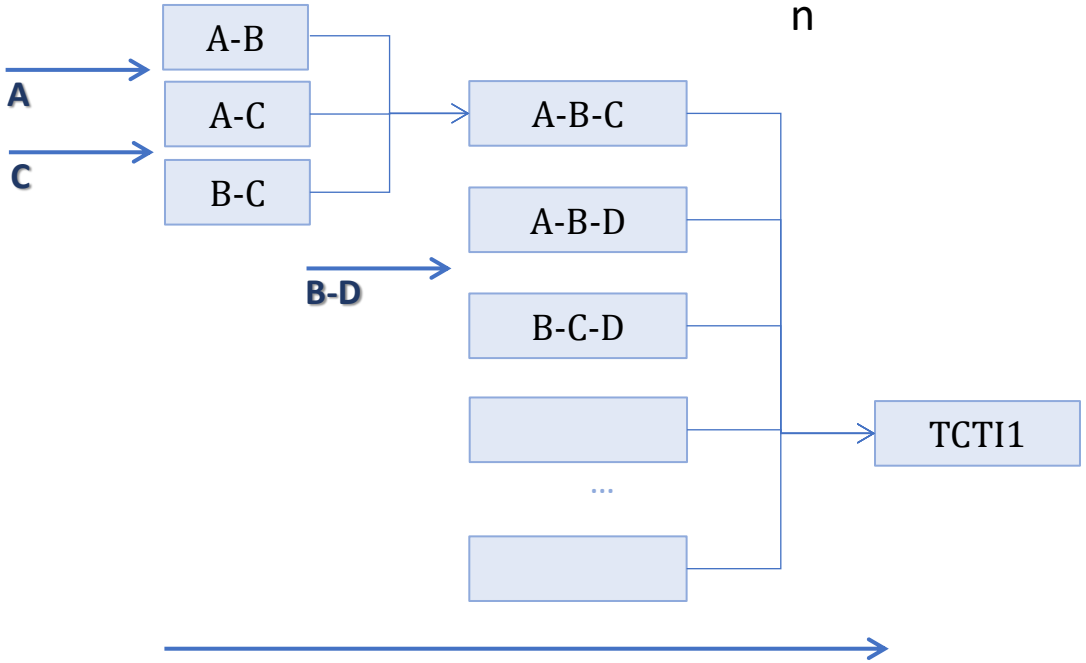
$$ {}^{E}G_m^{\alpha} = \sum_{i\neq j} x_i x_j L_{i,j}^{\alpha} + \sum_{i\neq j\neq k} x_i x_j x_k L_{i,j,k}^{\alpha} + \sum_{i\neq j\neq k\neq l} x_i x_j x_k x_l L_{i,j,k,l}^{\alpha} + \cdots $$



Phase based approach to modelling the underlying thermodynamics and phase equilibria of a system through a self consistent framework.

❑ Advantages

- Efficient and versatile
- Self-consistent and elimination of data uncertainty
- Prediction for regions (temperature/composition) where data is not available or difficult/impossible to obtain
- Based on unary, binary and ternary data, we can predict properties of multicomponent systems, e.g. real engineering materials
- Capture composition, temperature and pressure dependence.

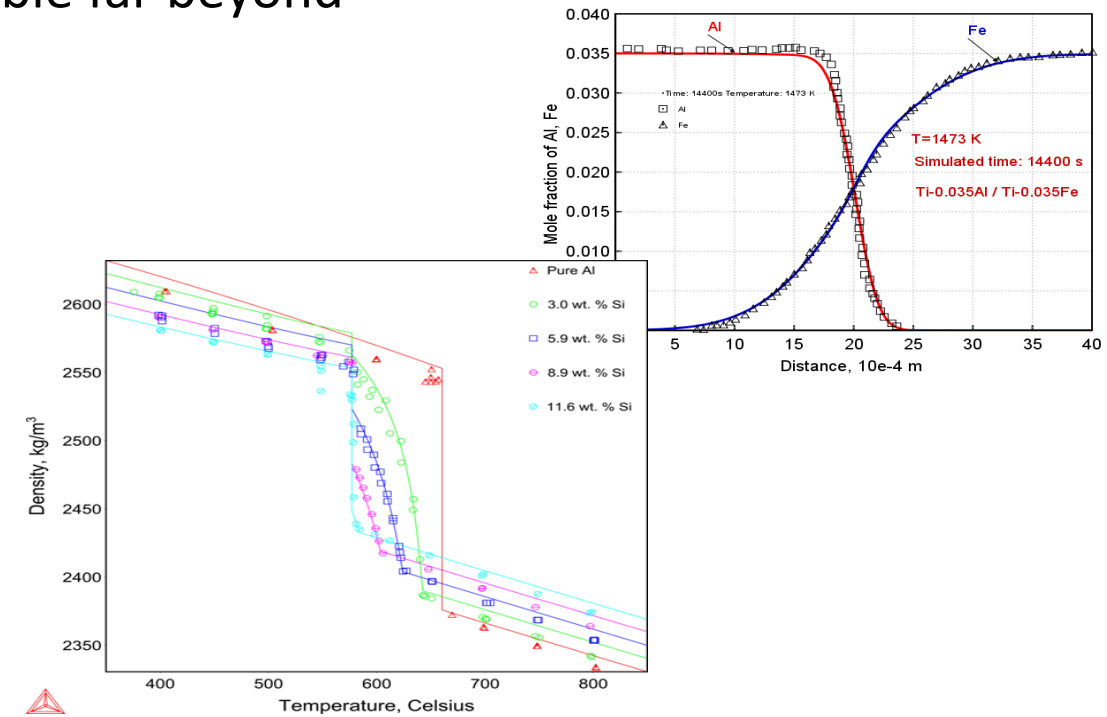


During extrapolations to higher order systems

- Inconsistencies can be eliminated.
- Over-/underestimations can be reduced.

CALPHAD extensions

Another advantage of CALPHAD is that it is Extendable far beyond traditional thermochemistry, e.g.

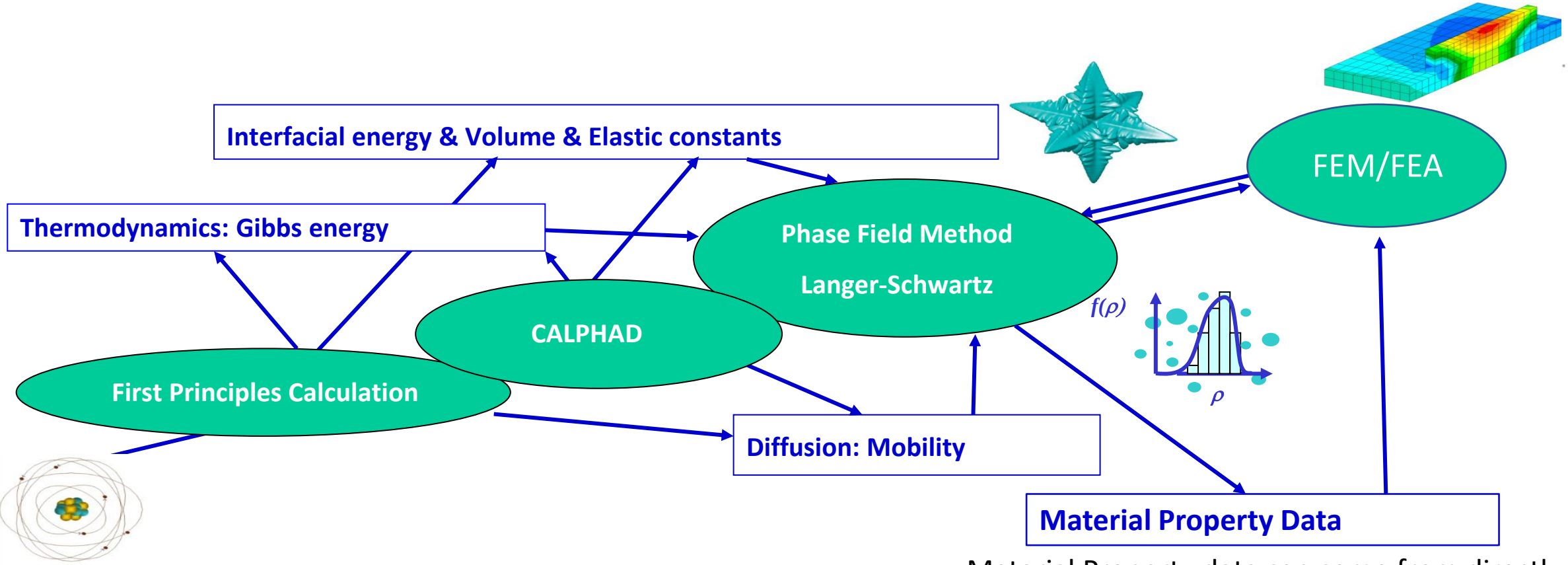


- **Atomic mobility**
- **Molar volume & Interfacial energy**
- Viscosity
- Thermal Conductivity/Diffusivity
- Electrical Conductivity/Resistivity
- Elasticity
  - Elastic constants, Young’s modulus, Bulk modulus, Shear modulus, Poisson's ratio
- Thermal radiative properties
  - Emissivity, Adsorptivity, reflectivity, transmissivity

CALPHAD – Bridging Atoms and Microstructure

Thermo-Calc Software

Towards prediction of microstructure evolution and material properties / mechanical behavior



Material Property data can come from directly from CALPHAD (e.g. density or specific heat), or through microstructure / property models (different for every material)

Simulation Software

Thermo-Calc

Minimization of the total Gibbs free energy under given conditions.

$$G = \sum_{\phi} N^{\phi} G_m^{\phi}\left(T, P, x_i^{\phi}\right)$$

$$\frac{\partial G}{\partial x_i^{\phi}} = 0$$

Diffusion Module (DICTRA)

1-D diffusion simulation - Numerically solve diffusion equations

Solve Diffusion

$$\frac{\partial \mathbf{c}}{\partial t} = -\frac{\partial}{\partial z}(\mathbf{J}) \quad \textbf{where} \quad \mathbf{J} = -\mathbf{D}\frac{\partial \mathbf{c}}{\partial z}$$

Precipitation Module (TC-PRISMA)

Mean field precipitation simulation – using LS (Langer-Schwartz) and KWN (Kampmann and Wagner Numerical) Approach

Continuity equation

$$\frac{\partial f(r,t)}{\partial t} = -\frac{\partial}{\partial r}\left[\upsilon(r) f(r,t)\right] + j(r,t)$$

$$C_0^{\alpha} = C^{\alpha} + \left(C^{\beta} - C^{\alpha}\right)\int_0^{\infty} \frac{4\pi}{3} f(r,t)\, r^3 dr$$

Mass balance

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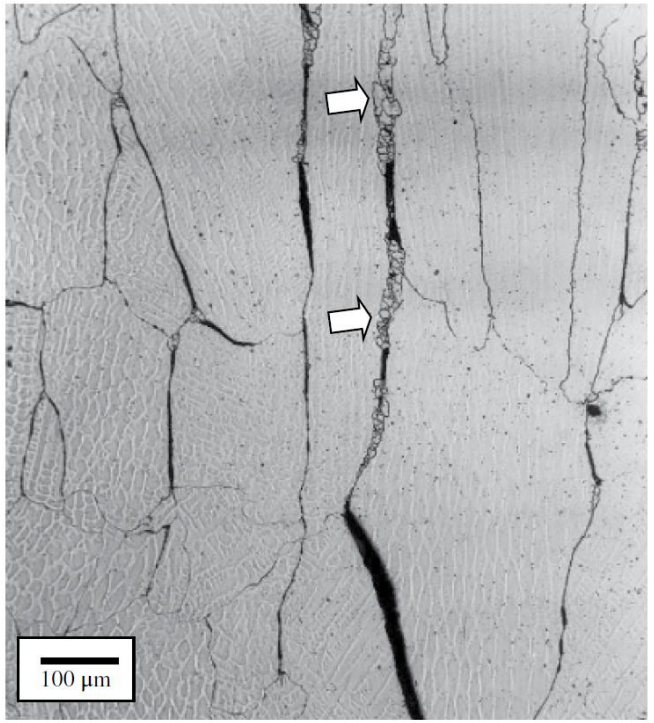
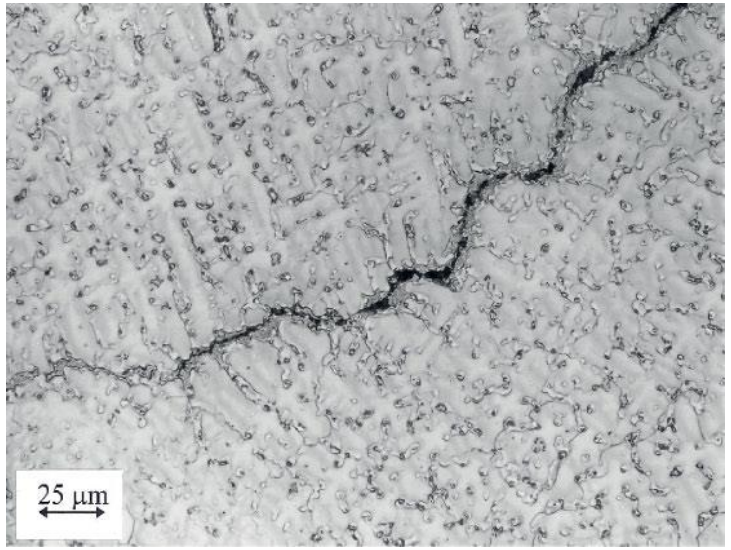
Materials Challenges in Additive

- Rapid solidification and reheating from laser/electron beam can drastically change material behavior
  - Solidification Cracking
  - Ductility dip cracking
  - Strain-Age Cracking (typically from gamma prime)
  - Undesirable precipitates can form (due to reheating cycles)
  - Meta-stable phases can form





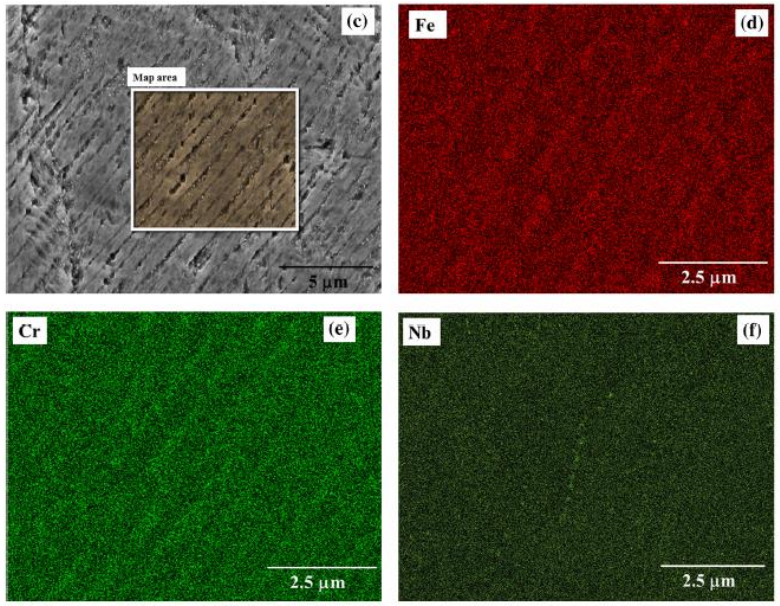
Left: Solidification crack along solidification grain boundary in Ni-base alloy weld

Right: Ductility dip cracks along migrated grain boundaries in Ni-base alloy multi-pass weld

Images from:
Lippold, John C. *Welding metallurgy and weldability*. John Wiley & Sons, 2014.

Materials Challenges in Additive

- Chemistry effects
  - Segregation due to solidification
  - Laser can cause vaporization of certain elements
  - Surface area of powder can cause introduction of oxygen
  - Non-noble cover gasses can ‘dissolve’ into melt pool (eg. N)
- Residual Stress
  - Material properties (eg. Density) are not always known for metastable phases or novel compositions
- Many alloys in use today were not designed for additive
  - Many powders designed for HIP (no solidification) or welding (slower cooling rates)
- How can we better predict current material behavior, or design new materials that are resistant to these problems or even take advantage of some aspects of the additive process
  - i.e. use the reheating to form a strengthening precipitate
  - Tailor location specific properties by using wash passes when needed to increase strength in particular areas



EDS Scans showing segregation of elements across dendrites in 17-4 PH Additive build

Cheruvathur et al "Additive Manufacturing of 17-4 PH Stainless Steel: Post-processing Heat Treatment to Achieve Uniform Reproducible Microstructure." JOM 68.3 (2016)

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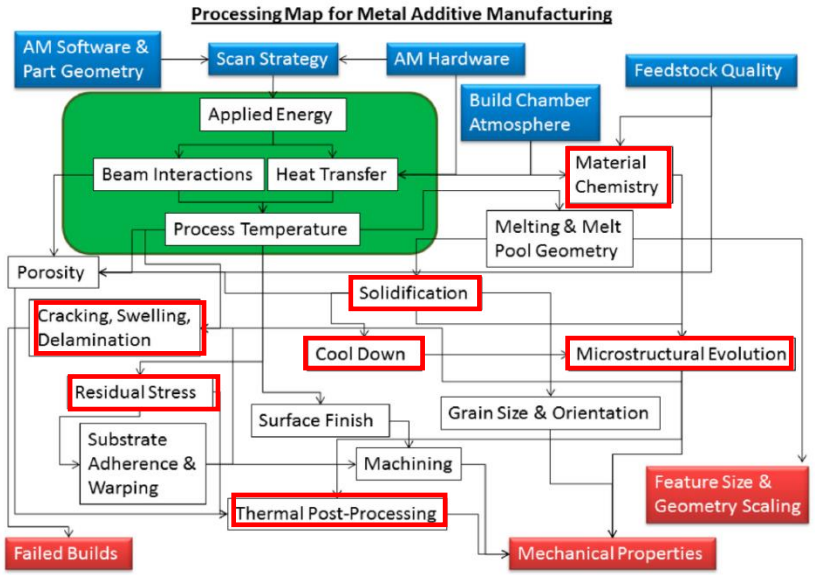
How CALPHAD based tools can be integrated into the processing map for AM



11 Focus of current review: overview of relationship between input parameters and underlying physics to meet the expected outcome of metal AM

Cool Down and Microstructural Evolution: Thermal cycles of the build can be used to predict extent of precipitation/dissolution of phases, which gives insight into final microstructure

W. J. Sames, F. A. List, S. Pannala, R. R. Dehoff & S. S. Babu (2016) The metallurgy and processing science of metal additive manufacturing, International Materials Reviews, 61:5, 315-360,

Material Chemistry: Used as an input to CALPHAD calculations

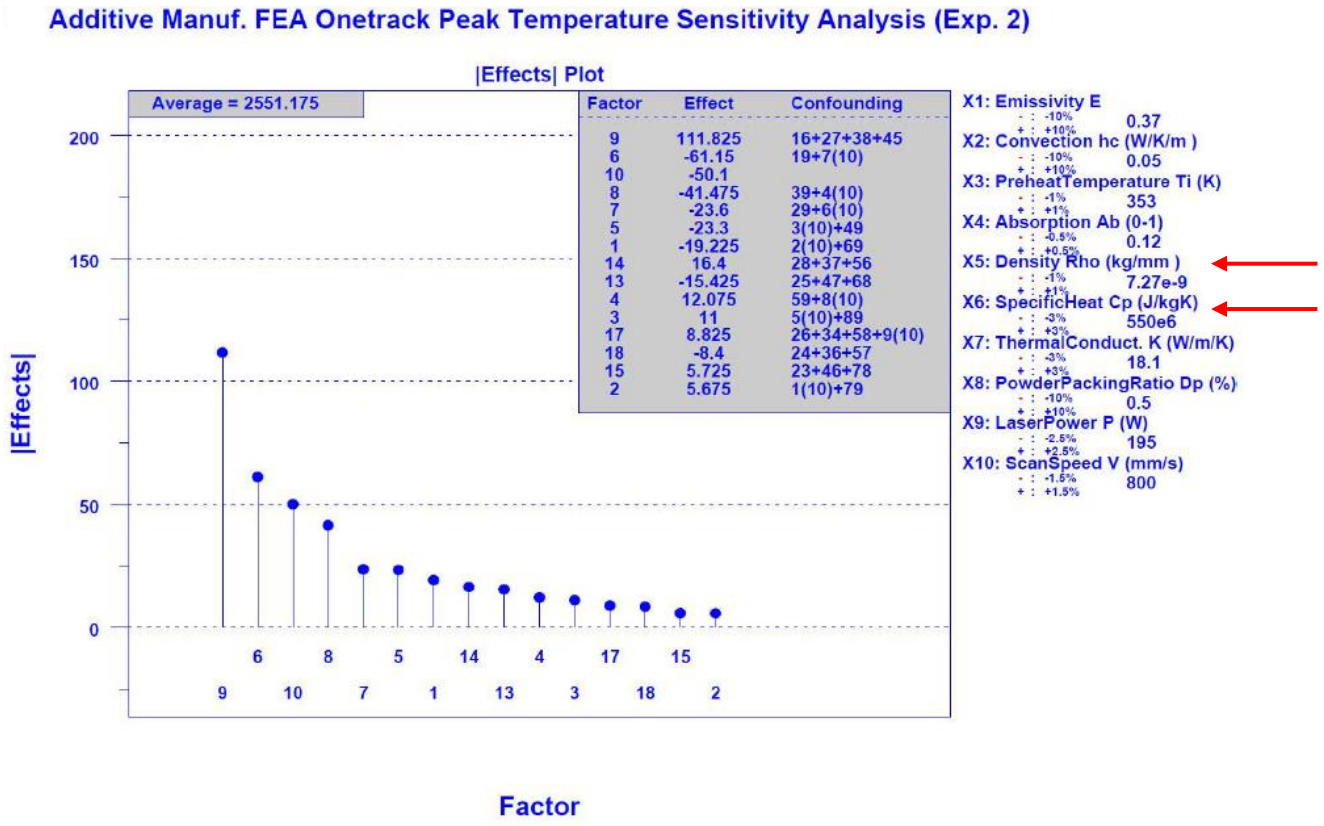
Solidification: Scheil can predict compositional segregation and phase formation, solidification temperatures, latent heat of evolution, volume change (shrinkage) etc. during the solidification process

Cracking, Swelling, Delamination: Many possible types of cracking, but solidification cracking and other types of precipitation induced cracking may be able to be predicted or alloys ranked with CALPHAD tools

Residual stress: can obtain thermal expansion data from CALPHAD tools, used in FEA to determine stresses based on thermal gradients

Thermal Post Processing: Optimum post processing times and temperatures can be predicted using CALPHAD tools, using nominal and/or segregated chemistries as inputs. Can be used for homogenization or precipitation treatments to assist in optimization of properties

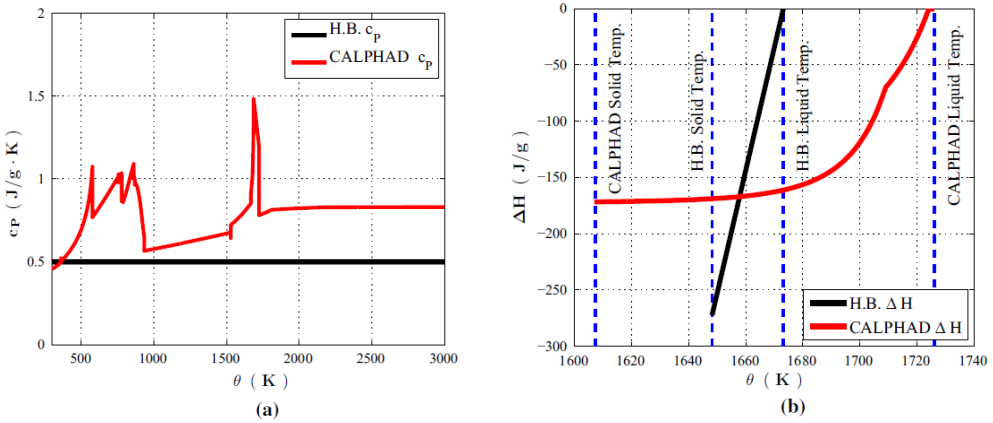
What parameters are important in FEA modelling?



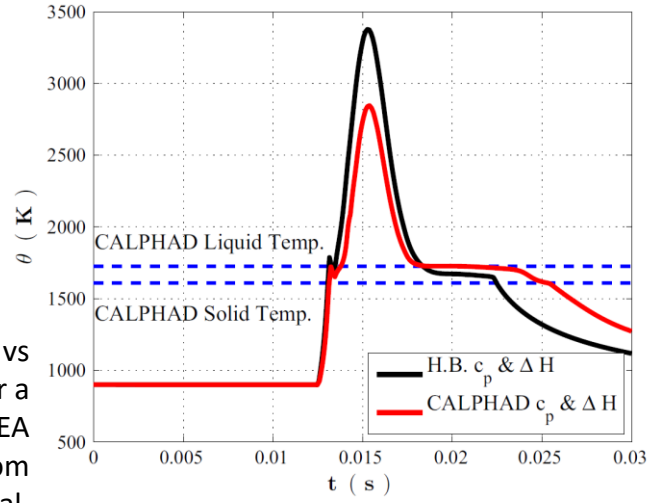
Ma, Li, et al. "Using design of experiments in finite element modeling to identify critical variables for laser powder bed fusion." *2015*

Applications to mechanical/thermal FEA modeling

- Data is not always available for specific heats of material
- General ‘alloy’ data may be available from a handbook, but this is usually a constant value
- How do you tweak your model when the chemistry of your material is different heat to heat?
- Properties like specific heat, density, enthalpy, mobilities, latent heat can be calculated as a function of chemistry and temperature - and used as inputs into other codes to determine heat transfer, stress distributions etc.
- Comparison from Smith et al. of calculated specific heat and enthalpy change vs handbook value for a 316L stainless steel – note over 500K change in peak temperature prediction, as well as 2x change in solidification time – this also has an effect on weld pool geometry

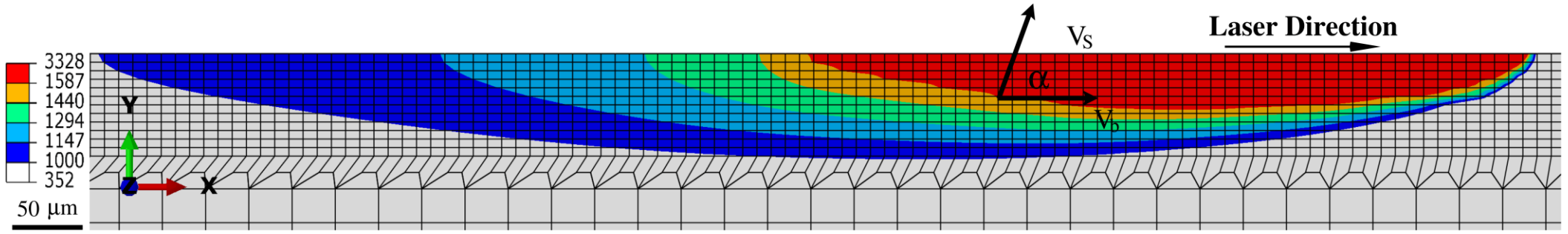


Comparison of handbook values and CALPHAD calculated values of Cp (left) and ΔH (right) – from Smith, et al. / *Computational Mechanics* 57.4 (2016): 583-610.

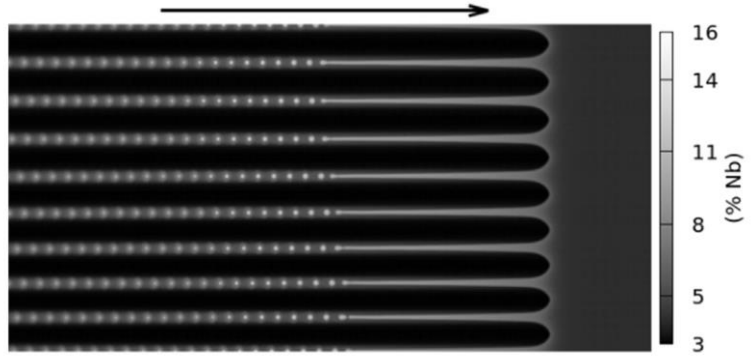


Resulting temperature vs time predictions for a selected node in an FEA simulation – also from Smith, et al.

Applications to mechanical/thermal FEA modeling



- Keller et al. used a transient thermal model in ABAQUS to model one layer of powder deposition of laser melted Alloy 625 powder.
- Specific heat capacity and density were taken as functions of temperature from a Thermo-Calc Scheil simulation and used as inputs in the ABAQUS model.
  - This allows for the full effect of segregation during solidification, and possible eutectic phase formation (NbC, Laves) to be taken into account in the Cp and density values.
- From this – the pool shape and resulting solidification speed Vs = V_{laser}*cos(α) can be determined along with thermal gradient G
- These two values are needed for a phase field simulation to predict the dendrite arm spacing
- Keller also simulated this, found reasonable agreement of dendrite arm spacing



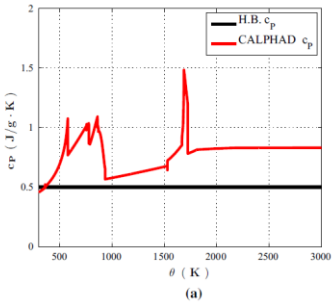
Phase field simulation of cellular dendrite structure (brightness = wt% Nb)

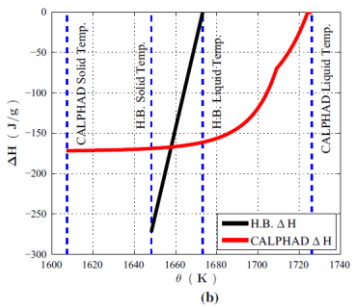
Keller, Trevor, et al. "Application of finite element, phase-field, and CALPHAD-based methods to additive manufacturing of Ni-based superalloys." *Acta materialia* 139 (2017): 244-253.

Applications to mechanical/thermal FEA modeling

- an Integrated Computational Materials Engineering (ICME) Case Study

- Each tool complements each other and improves the result in the next step of the process





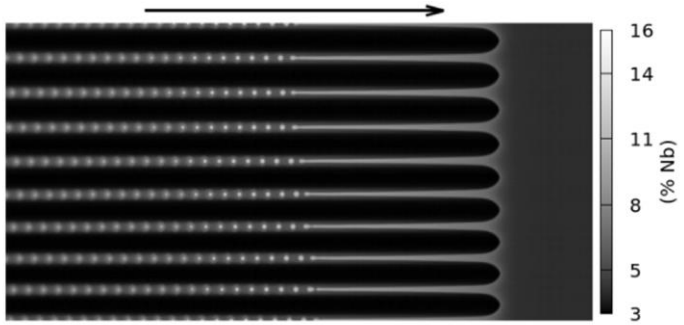
CALPHAD

Gibbs energy, mobility

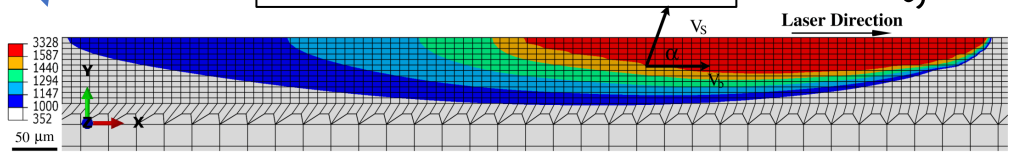
Density,
Specific heat,
Enthalpy, etc

Finite Element

Thermal
Gradient &
solidification rate



Phase Field



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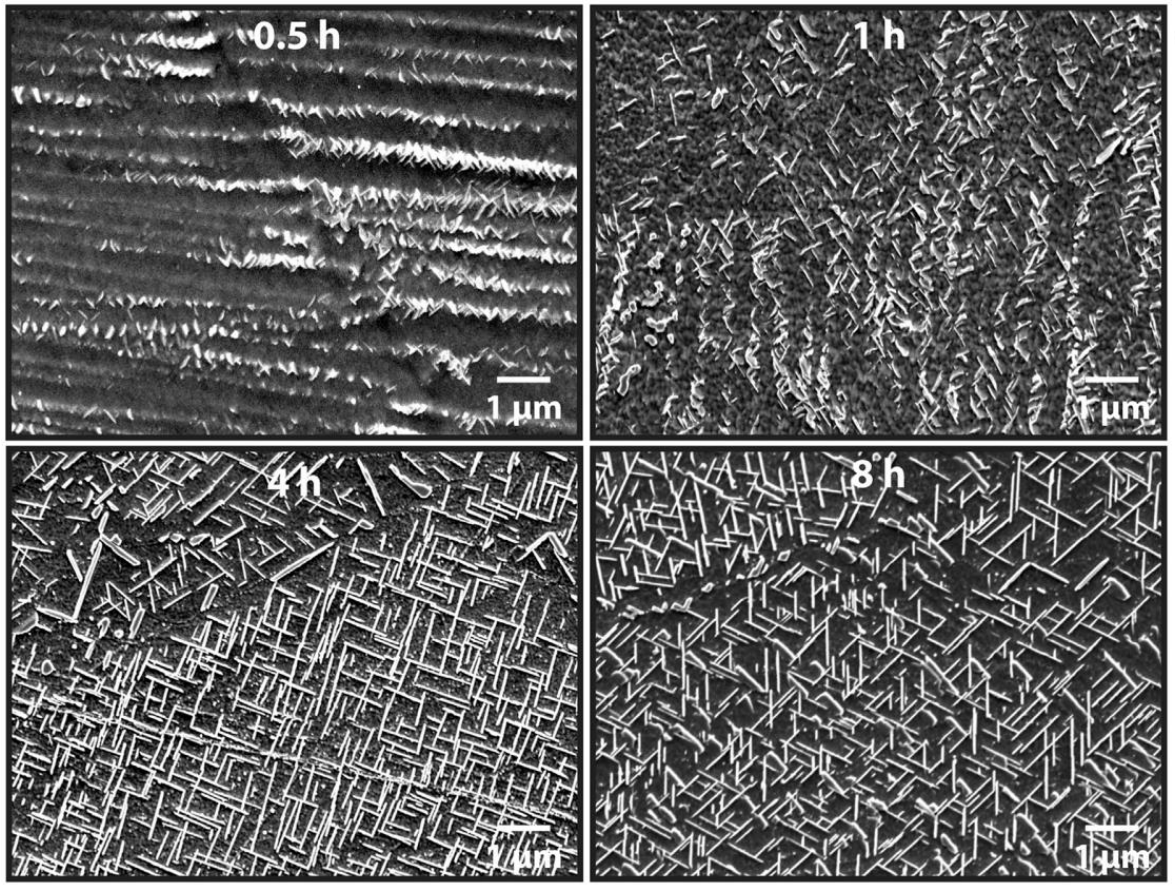
Applications to metallurgical phenomena - Alloy 625 Problem

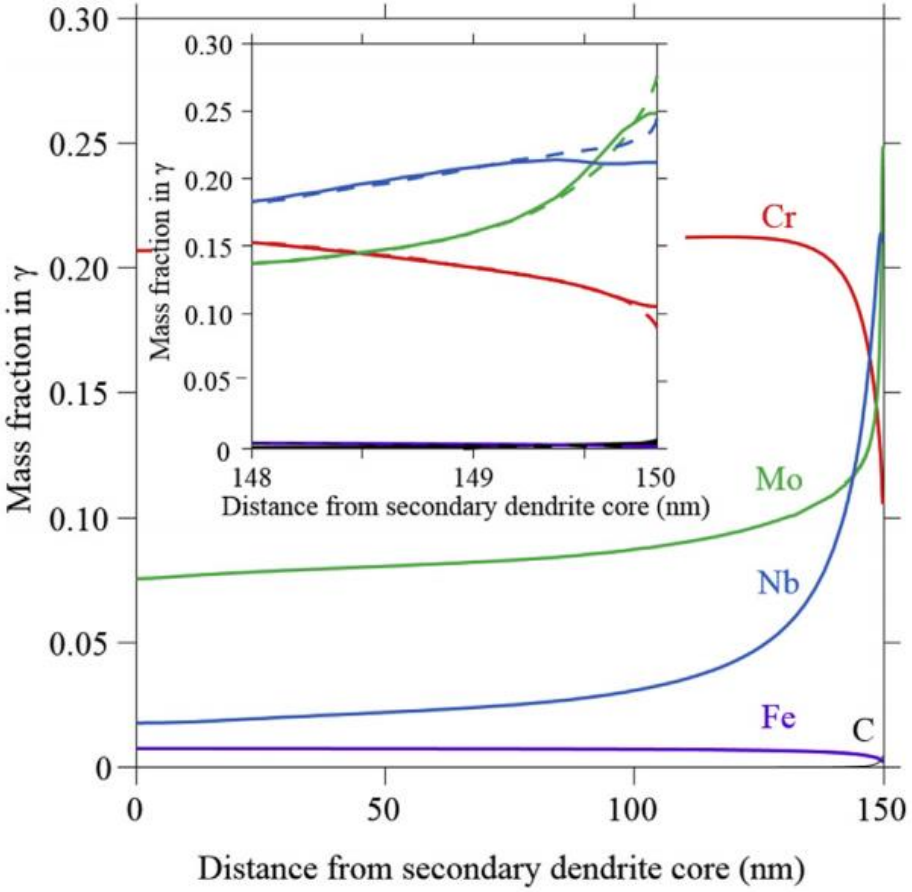
- Standard ‘stress relief’ treatment at 870°C causes copious precipitation of delta phase (deleterious), even after 30 minutes (atypical)
- Micrographs from Zhang et al. reveal that the delta phase starts to precipitate in the inter-dendritic regions, where DICTRA predicted higher Nb and Mo due to segregation
- Further heat treatment causes coarsening of the delta phase
- At first glance, it looks like this may be caused by solidification segregation – can we model this?



Zhang, Fan, et al. "Effect of heat treatment on the microstructural evolution of a nickel-based superalloy additive-manufactured by laser powder bed fusion." Acta Materialia (2018).

Applications to metallurgical phenomena - Alloy 625 Solidification

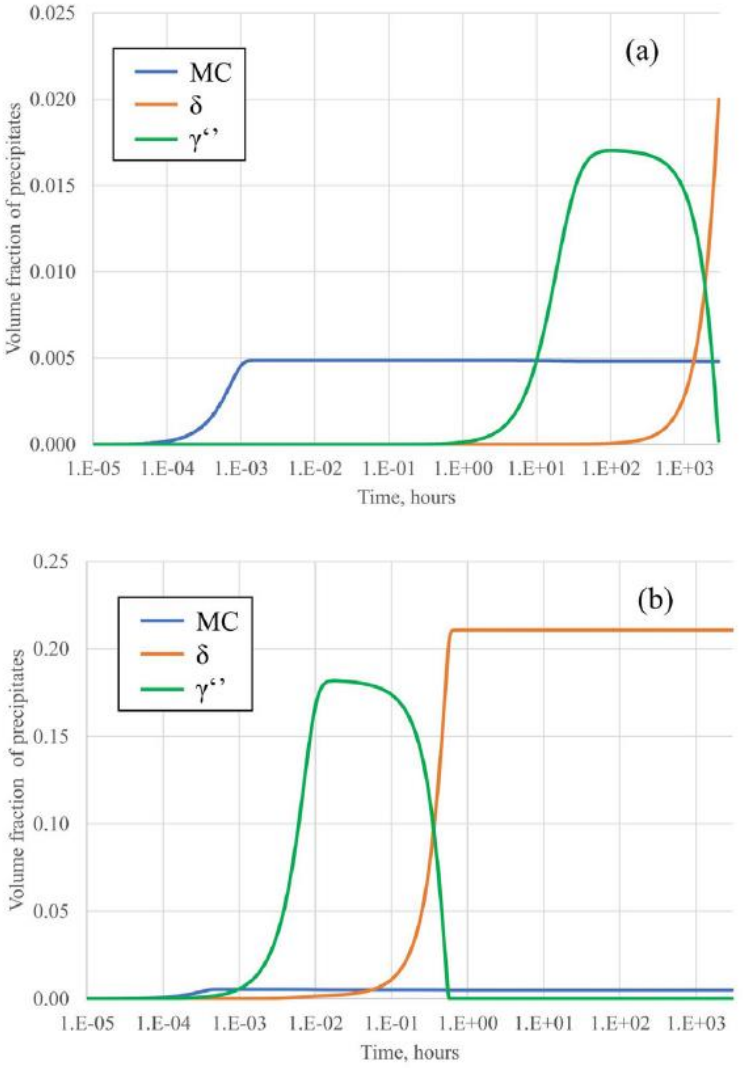
- Scheil predicts the most extreme segregation
- DICTRA can be used to simulate the back diffusion during cooling, as well as diffusion during reheat cycles
- Keller et al. simulated the segregation for 3 consecutive scan passes
  - Pass 2 re-melted the area of study (reset the segregation effectively) and is shown as the dashed line
  - Pass 3 caused reheating close to melting, and some diffusion to occur (solid line)
  - Authors found that subsequent passes were not of high enough temp/long enough time to cause significant diffusion
  - Reheating from subsequent passes is insufficient to homogenize the segregation



Keller, Trevor, et al. "Application of finite element, phase-field, and CALPHAD-based methods to additive manufacturing of Ni-based superalloys." *Acta materialia* 139 (2017): 244-253.

Applications to metallurgical phenomena - Alloy 625 Precipitation

- Zhang et al. also performed TC-PRISMA simulations on two different representative compositions at 870°C
  - (a) from the dendrite core
  - (b) from the dendrite boundary/interdendritic region
- In both cases, gamma double prime forms first, then dissolves in favor of the delta phase (expected)
- The kinetics are sped up greatly for the segregated composition (increased Mo and Nb)
  - This lines up with what is seen in the 30 minute heat treatment
- Authors suggest performing a homogenization heat treatment above the delta solvus in a single phase region (determined with Thermo-Calc to be around 1150°C)
  - This may increase grain size, so more investigation is needed



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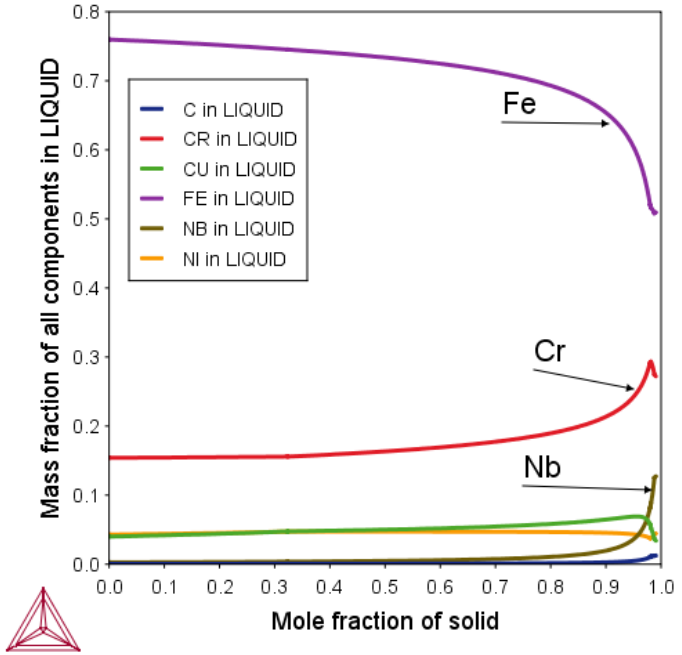
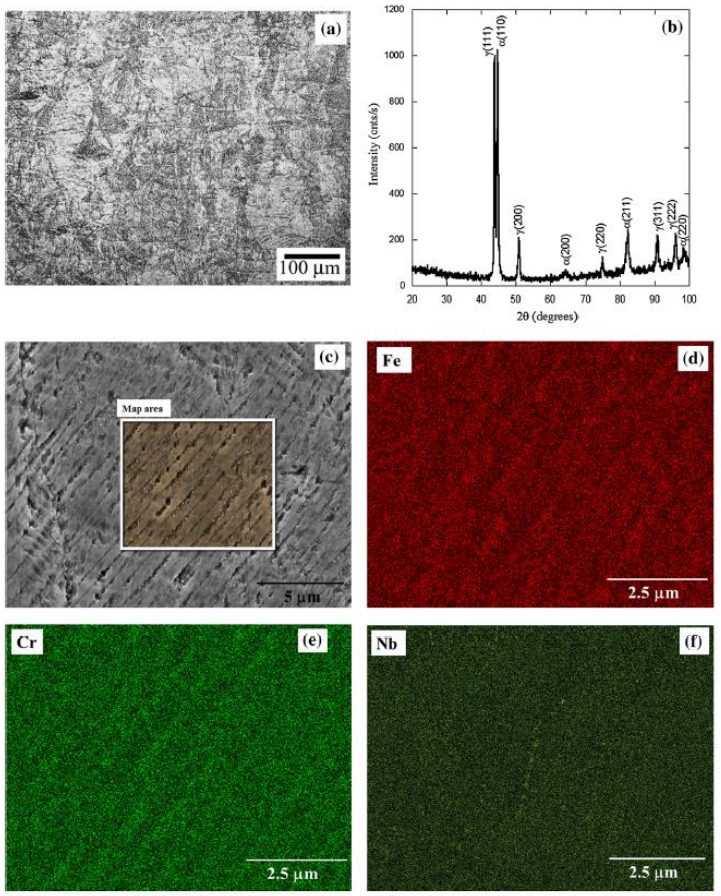
Applications to metallurgical phenomena - Solidification of 17-4PH

- 17-4 PH is a martensitic stainless steel
- Segregation during solidification (and potential nitrogen pickup) causes local depression of Ms temperature (to below room temp)
- Significant volume fraction of retained austenite in as built condition
- Potentially detrimental to properties (alloy is supposed to be fully martensitic)



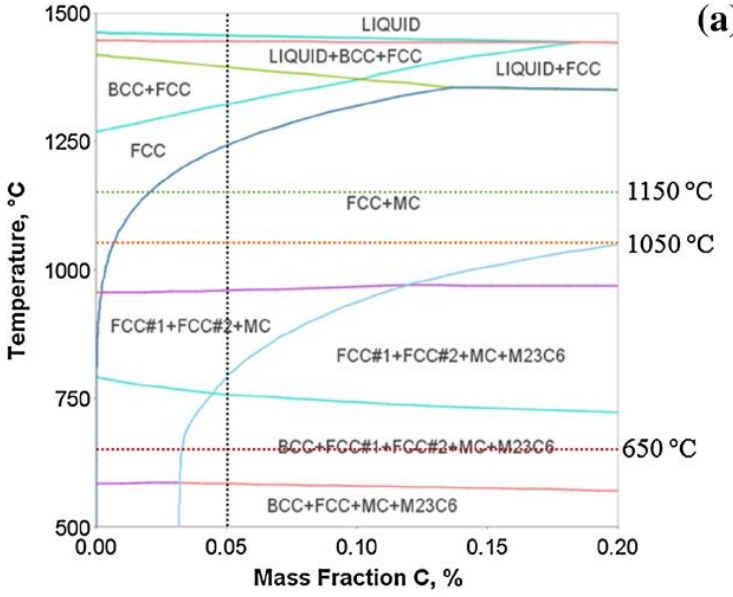


Above: Scheil simulation in Thermo-Calc showing segregation of elements during solidification
Right: XRD scan on As-built condition showing retained austenite, EDS map across dendrites showing segregation of elements

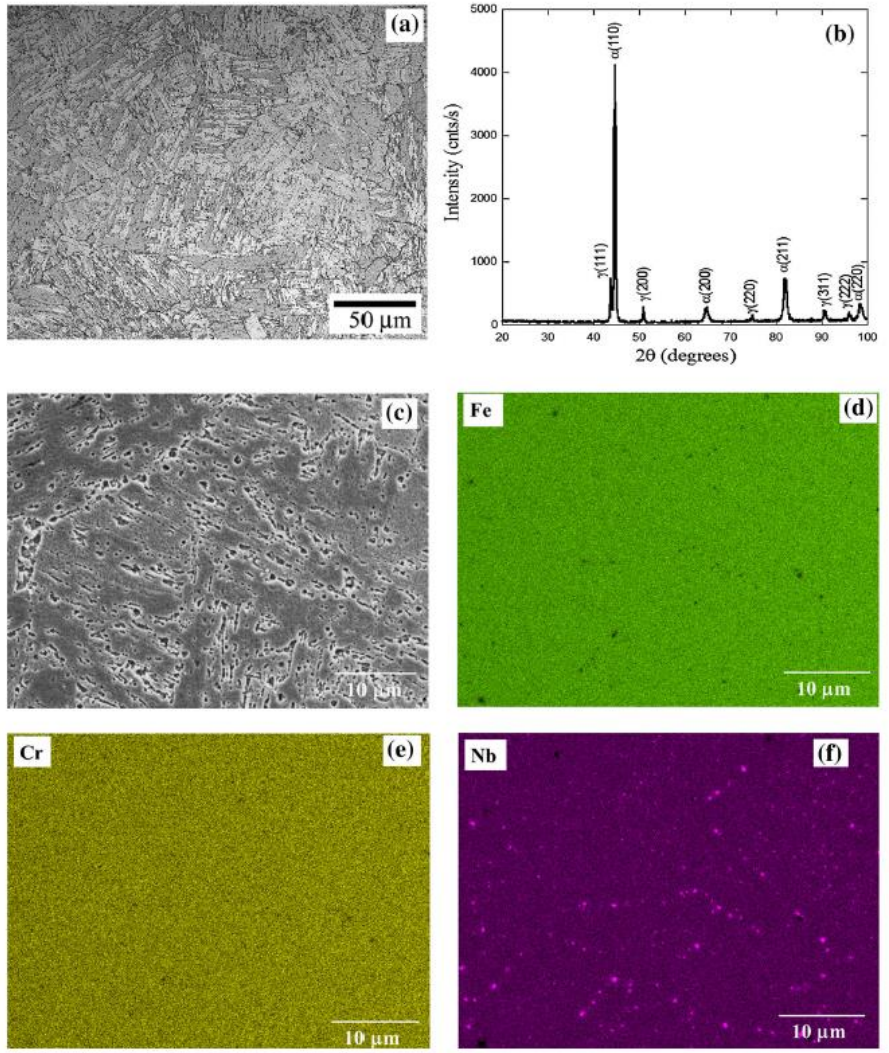
Cheruvathur et al "Additive Manufacturing of 17-4 PH Stainless Steel: Post-processing Heat Treatment to Achieve Uniform Reproducible Microstructure." JOM 68.3 (2016)

Applications to metallurgical phenomena - Solidification of 17-4PH

- Isoplethal sections of the phase diagram for the alloy can be made to determine optimum temperatures for heat treatment
- Homogenization heat treatment was performed post build and the volume fraction of retained austenite decreased significantly.
- Bright Nb spots are MC (NbC) carbides which was predicted by Thermo-Calc
- unable to fully homogenize – because NbC is stable to high temperatures!



Above: Isopleth section showing that even with variation in carbon, a large FCC+MC carbide region can be found to perform homogenization treatment
Right: XRD scan on heat treated build, along with EDS maps of the microstructure.



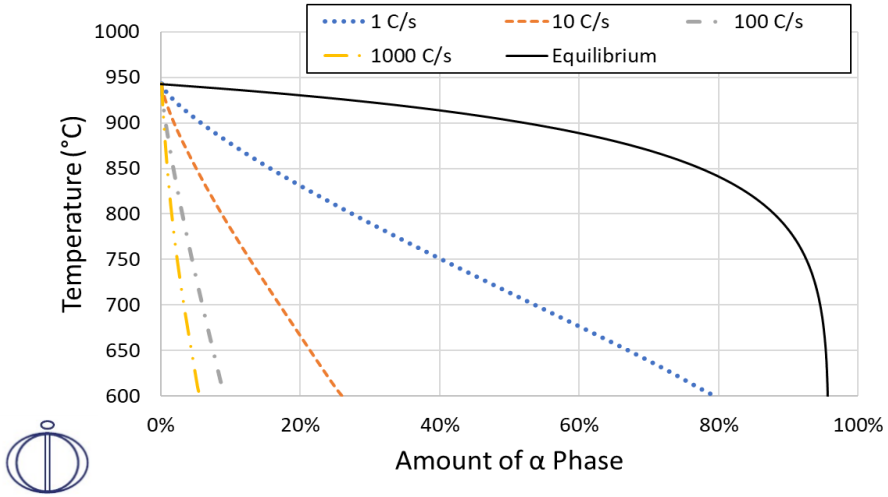
Cheruvathur et al "Additive Manufacturing of 17-4 PH Stainless Steel: Post-processing Heat Treatment to Achieve Uniform Reproducible Microstructure." JOM 68.3 (2016)

Outline

- Introduction
- Background on CALPHAD tools
- Materials challenges with additive manufacturing
- Applications to mechanical/thermal FEA modeling
- **Applications to metallurgical phenomena**
  - Alloy 625 Case study
    - Stress relief heat treatment promotes delta phase
  - 17-4 PH Case study
    - Predicting solidification behavior
    - Subsequent heat treatment
  - **Ti-6Al-4V Case study**
    - **Predicting phase balance & microstructure morphology**
  - Cracking Prediction Methods
    - Solidification, Liquation, Solid State
- Conclusion / Future Directions

Applications to metallurgical phenomena - Phase balance in Ti-6-4

- Ti alloys – alpha/beta phase balance important for mechanical properties
  - balance creep, fracture toughness, strength, ductility
- Martukanitz et al. simulated the amount of alpha phase in a Ti-6Al-4V alloys using Thermo-Calc and DICTRA as a function of cooling rate from 950°C.
- Further heating and cooling cycles will cause the alpha phase to grow and shrink depending on the temperature.
- If the full thermal history is known this can be simulated using DICTRA to determine the final volume fraction of phase

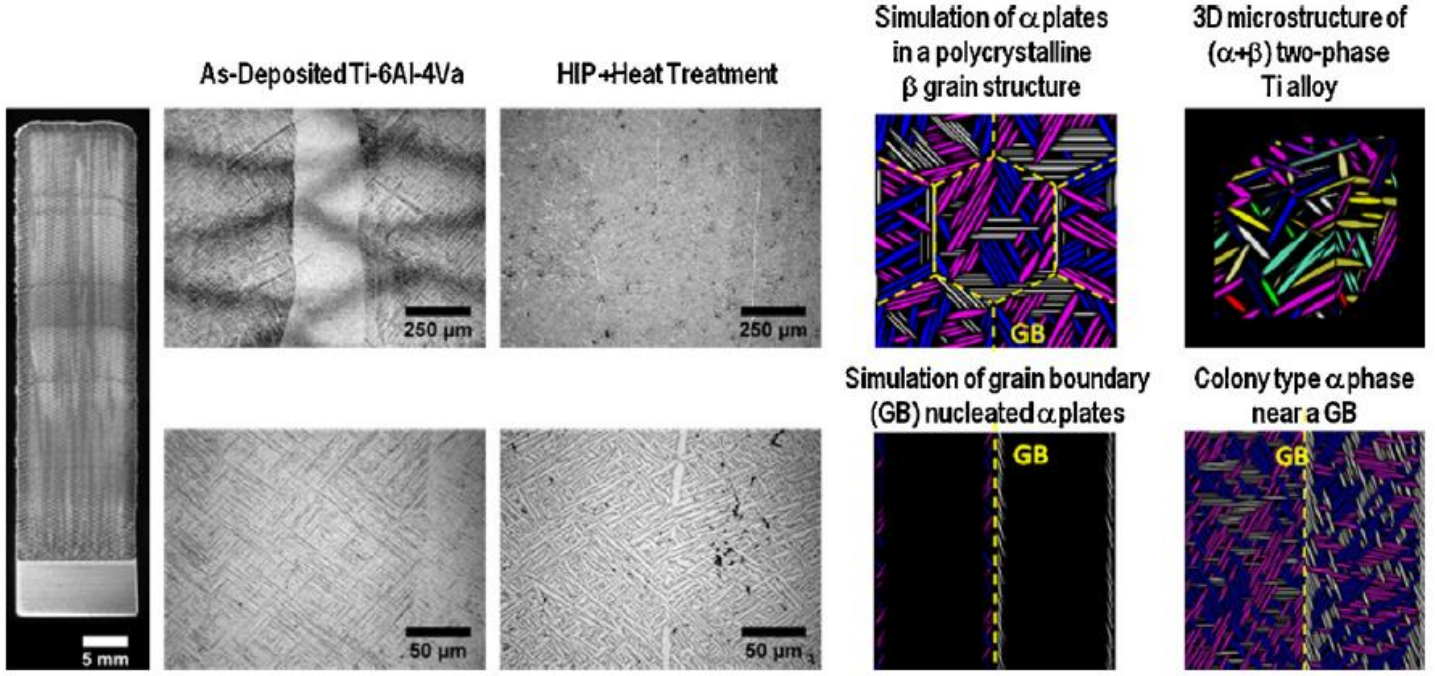


Calculated phase fraction of alpha for a B homogenized Ti-6-4Al alloy during continuous cooling through diffusion controlled simulations.

Figure recalculated based on: R. Martukanitz et al. Toward an integrated computational system for describing the additive manufacturing process for metallic materials / *Additive Manufacturing 1–4 (2014) 52–63* 61

Applications to metallurgical phenomena - Morphological Prediction

- Morphology of α/β in Ti alloys critical for property balance
  - Basketweave, colony alpha, GB alpha
- Thermodynamic and mobility data from CALPHAD databases can be used in conjunction with phase field code (such as MICRESS) to make microstructure predictions based on a given composition and thermal history
- Martukanitz et al. demonstrated predicting colony α at grain boundaries during heat treatment



Example of phase field model compared with build microstructure – from *R. Martukanitz et al. / Additive Manufacturing 1–4 (2014) 52–63*

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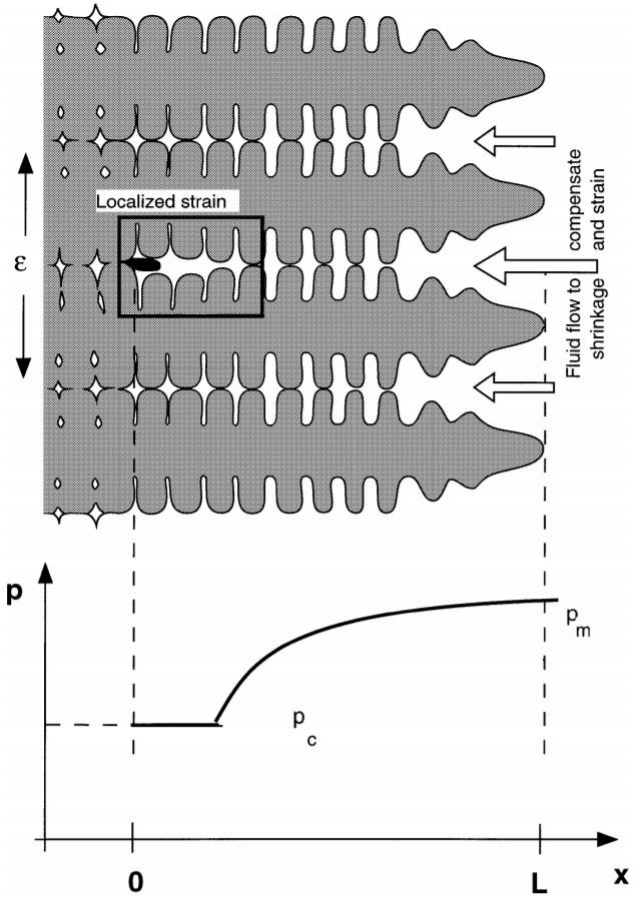
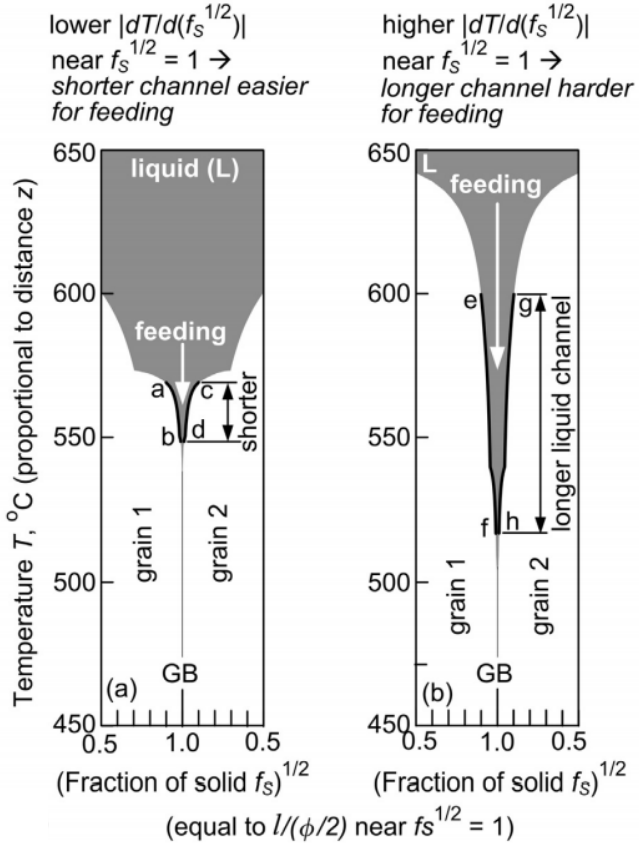
Applications to metallurgical phenomena - Solidification Cracking Prediction

- Many theories and methods
- Most consider the nature of the last liquid to solidify
- This can be predicted with Scheil (and back diffusion can be considered if needed)
- Can only rank alloys – but can help determine the nature of cracking



Rappaz, M., J-M. Drezet, and Met Gremaud. "A new hot-tearing criterion." *Metallurgical and materials transactions A*30.2 (1999): 449-455.



Kou, Sindo. "A criterion for cracking during solidification." *Acta Materialia* 88 (2015): 366-374.

Applications to metallurgical phenomena - Liquation Cracking Prediction

- Liquation can occur at fast heating rates
- Particles (such as NbC/gamma prime) can start to dissolve, but elements cannot diffuse away fast enough, locally suppressing melting temperature and causing local melting below the melt pool (in the heat affected zone) – combined with residual stress can cause a crack
- Liquation an be predicted at different thermal-cycles/heating rates with DICTRA

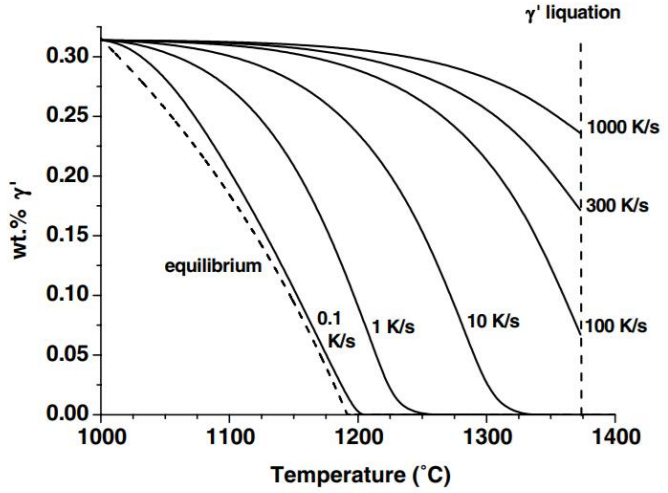


Fig. 3. Evolution with temperature of the relative amount of γ′ during heating at different rates.

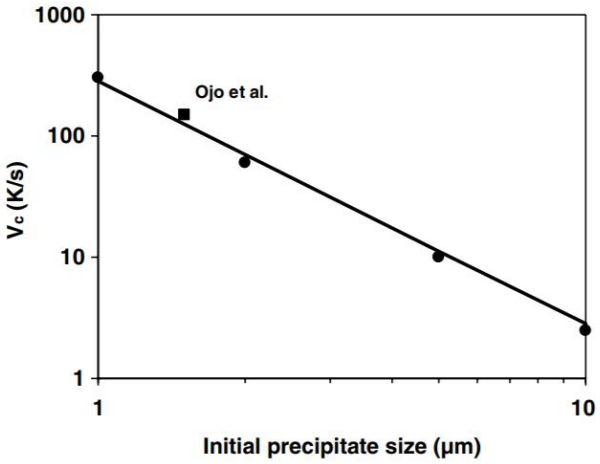
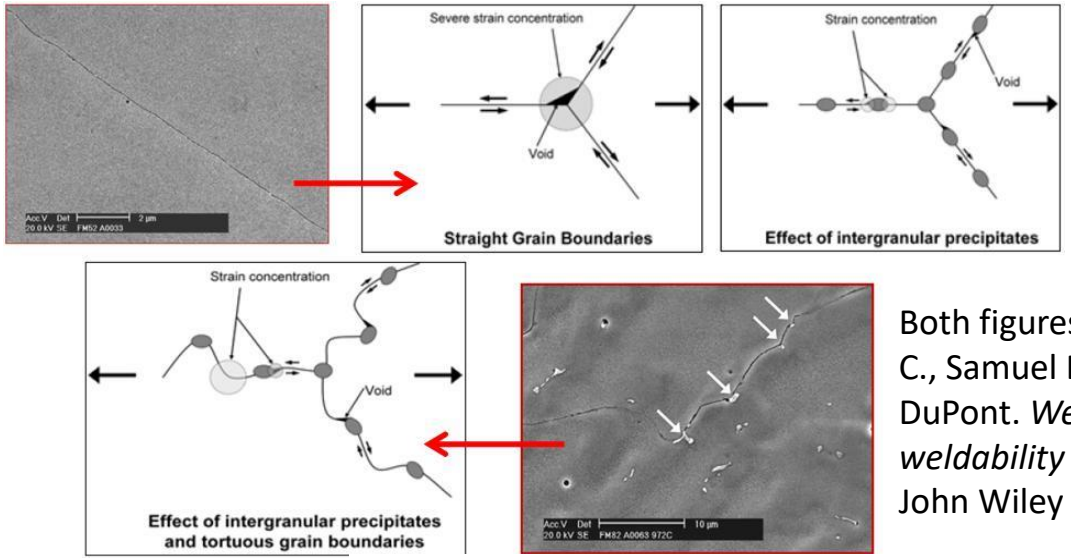


Fig. 5. Variation of the critical heating rate for γ′ liquation, V_c, with initial precipitate size.

Tancret, F. "Thermo-Calc and Dictra simulation of constitutional liquation of gamma prime (γ') during welding of Ni base superalloys." *Computational Materials Science* 41.1 (2007): 13-19.

Applications to metallurgical phenomena - Solid State Cracking Prediction

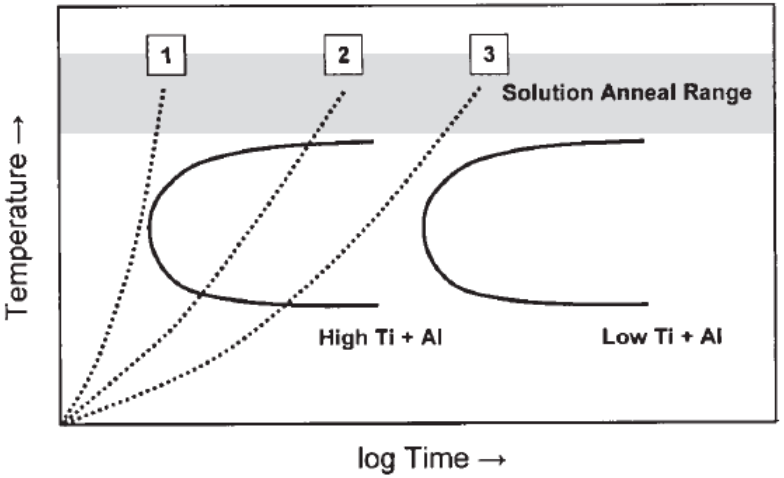
- Many different types of solid state cracking
  - Ductility dip, strain-age, stress relaxation, hydrogen, stress corrosion
- Many related to precipitation behavior (strengthening phases/carbides)
- Precipitation behavior can be simulated with TC-PRISMA, as a function of thermal cycling
- Allows insight into whether precipitates may form during build or post build heat treatments / composition modifications to avoid



Both figures from: Lippold, John C., Samuel D. Kiser, and John N. DuPont. *Welding metallurgy and weldability of nickel-base alloys*. John Wiley & Sons, 2011.

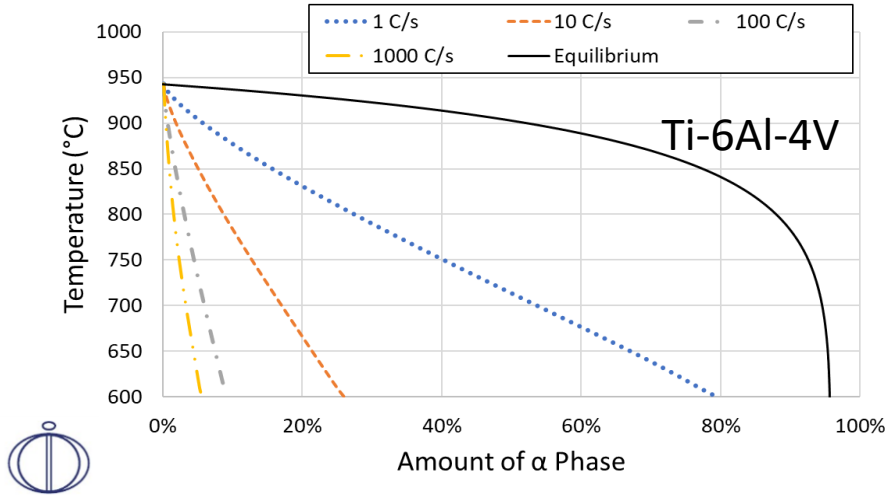
Above: DDC Mechanism

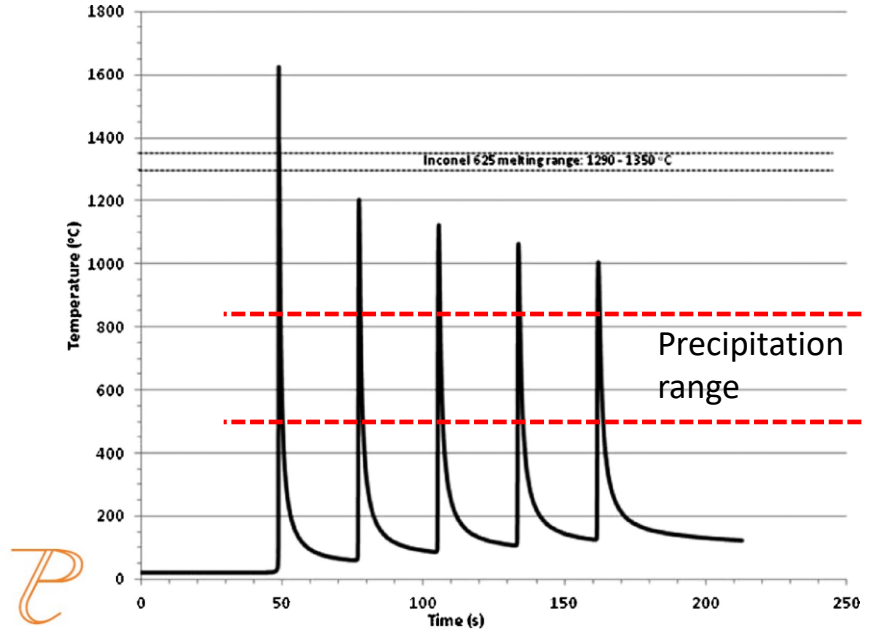
Right: Schematic of TTT curves for Ni-Superalloys and Heating rates required to avoid Strain-Age Cracking



Potential for Alloy Development

- Lots of room for alloy development
  - Current alloys designed for cast/wrought/forged processes
  - Potential to adjust chemistry to achieve optimum microstructure
  - Location specific properties
- Alloys with allotropic transformations (ex. steel/titanium)
  - Chemistry and cooling rate to optimize final phase balance
- Alloys that rely on precipitation
  - Could design to take advantage of repeated thermal cycles
  - Tailor scan strategy to precipitate more in areas that need more ductility





Above figures adapted from: R. Martukanitz et al. Toward an integrated computational system for describing the additive manufacturing process for metallic materials / *Additive Manufacturing 1–4 (2014) 52–63* 61

Compositionally Graded Joints/Builds

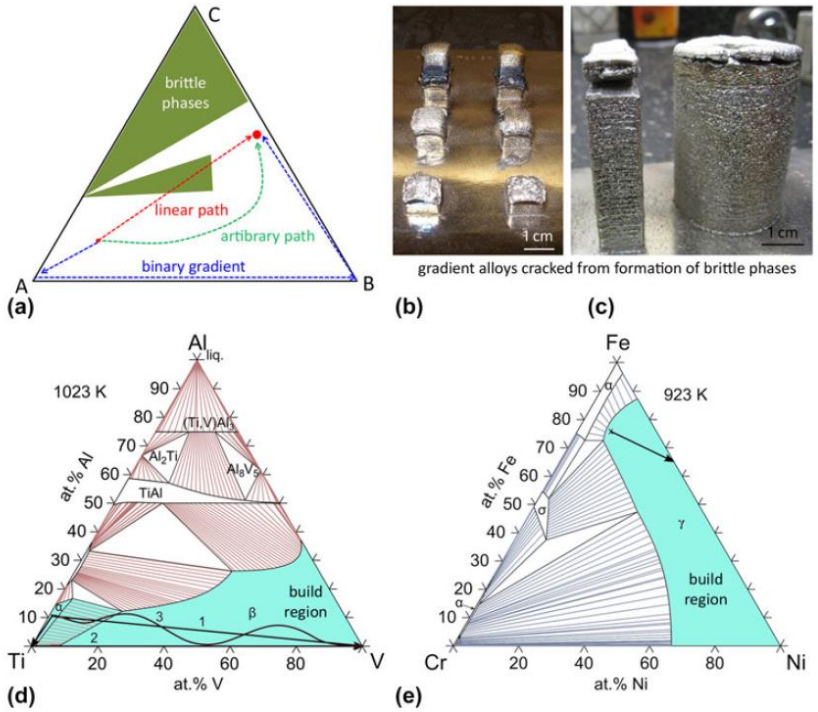


FIG. 4. (a) A schematic of a ternary phase diagram showing possible gradient paths from one alloy to another across a three-element phase space. Several routes are possible, based on factors such as the avoidance of brittle phases. (b, c) Gradient alloys which cracked during fabrication. (b) A failed gradient from Ti to Invar and (c) a failed gradient from Ti to 304L stainless steel. (d) A calculated Al–Ti–V phase diagram showing a gradient from Ti–6Al–4V to pure V showing three different gradient paths: (1) a linear gradient, (2) removing Al and then performing a binary Ti–V gradient, (3) an arbitrary path. The blue region is calculated to be free of brittle intermetallic phases and is comprised of hcp and bcc phases. (e) A calculated phase diagram for the Fe–Ni–Cr system showing a gradient from 304L stainless steel to Invar 36. In this diagram, the blue region has been calculated to be all single phase austenite, which simplifies the build due to the absence of brittle phases.

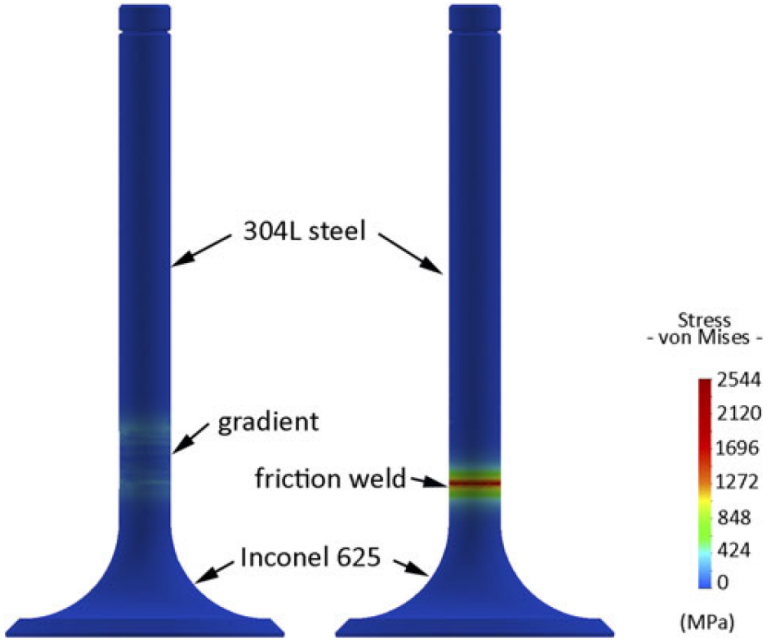


FIG. 5. A finite element model showing elastic mismatch in two dissimilar metal automobile valve stems at 1000 K. The figure on the left shows a valve with a 304L stainless steel stem connected to an Inconel 625 valve via a 2.5 cm long gradient of composition. On the right, the gradient is replaced with a friction weld. The stress at the joint of the friction welded part has an approximately ten times higher stress than the compositionally graded alloy.

Avoid brittle phases

Reduce sharp property gradients

D.C. Hofmann et al.: Compositionally graded metals: A new frontier of additive manufacturing J. Mater. Res., Vol. 29, No. 17, 2014

Conclusions

- CALPHAD based computational tools have been demonstrated to have many applications to additive manufacturing processes
- Thermodynamic and thermophysical data can be extracted and used to improve FEA type models
- By breaking down the process into different parts, many things related to microstructure evolution or metallurgical phenomena can be predicted and better understood
  - Solidification behavior (segregation, solidification temperatures, fraction solid)
  - Re-heating during subsequent layer deposition (precipitation, diffusion)
  - Post build heat treatments (homogenization, diffusion, precipitation)
- No ‘one size fits all approach’ – all alloys are different - a comprehensive combined experimental / computational approach should always be taken

Future Development

- FEA modeling of Additive manufacturing has highlighted a need for better material property data to be used as inputs to these models
- Need for other properties that we don't currently predict to improve FEA models
  - Viscosity & surface tension (for fluid flow)
  - Density for some metastable phases (for better residual stress predictions)
  - Thermal conductivity (for heat transfer/fluid flow/residual stress)
  - Martensite Start/Finish
- Thermo-Calc actively working on developing CALPHAD-type models for these properties