A personal perspective on the intersection between materials science and the research priorities of industry and government

David StJohn

The University of Queensland

Advanced
Materials
Processing
And
Manufacturing

CAMS 2016

Intersection with industry versus career pathway

Position & Location	Topic	Industry engagement
PhD (UQ)	Peritectic Solidification	Comalco
Post-doc 1 (CANMET)	Modelling of melt flow	Foundry industry
Post-doc 2 (UQ)	Reduction of Fe oxides	BHP & CRA
Lecturer (RMIT)	Ceramics, ion implantation	Nilcra, BHP, Comalco
Lecturer (UQ)	Ceramics, solidification, steel	Nilcra Ceramics, BHP
Manager (CRA – ATD)	Wear, diamonds, refractories ..	CRA ATD
CEO (CAST CRC (UQ)), Chair in Solidification	Various, greater focus on the study of solidification	Comalco, AMC, Ford, Nissan, ADCA, BlueScope
Interim CEO, Board member (DMTC)	Titanium, manufacturing: land, sea and air platforms	BAE Systems, Thales, GKN, Sutton Tools, others
Director AMPAM & Director Major Projects (UQ) Emeritus Professor	Al-Zn coatings, Advanced manufacturing, Pb-free solders, Mg & Ti alloys, solidification, ultrasonics	Bluescope Steel, Cook Medical, Nihon Superior, Magontec, Baosteel

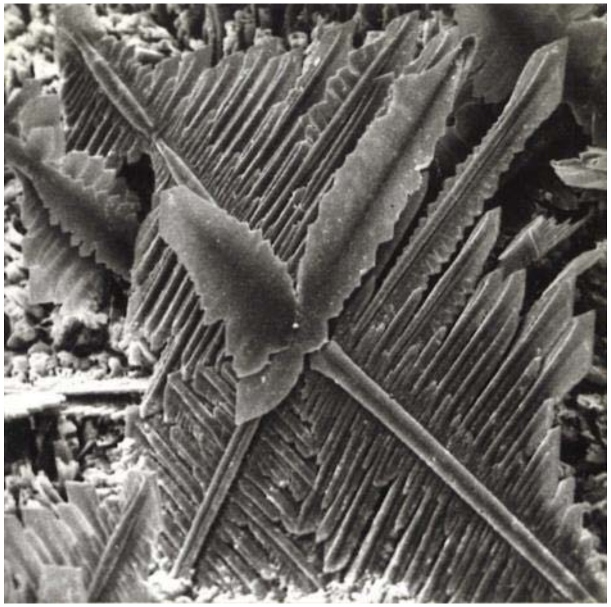
Role of government in assisting industry engagement

Position & Location	Topic	Government
PhD (UQ)	Peritectic Solidification	Commonwealth grant
Post-doc 1 (CANMET)	Modelling of melt flow	Canadian Fellowship
Post-doc 2 (UQ)	Reduction of Fe oxides	ARC Grant
Lecturer (RMIT)	Ceramics, ion implantation	GIRD grant
Lecturer (UQ)	Ceramics, solidification, steel	GIRD continued
Manager (CRA – ATD)	Wear, corrosion, refractories …	$$$ saved for CRA
CEO (CAST CRC (UQ)), Chair in Solidification	Various, greater focus on the study of solidification	CRC program, QLD RPP, QLD IBF, EIF → AEB
Interim CEO, Board member (DMTC)	Titanium, manufacturing: land, sea and air platforms	Defence Future Capability Technology Centres
Director AMPAM & Director Major Projects (UQ) Emeritus Professor	Al-Zn coatings, Advanced manufacturing, Pb-free solders, Mg & Ti alloys, solidification, ultrasonics	QLD Gov grants ARC DP and LP grants 2 Research Hubs European ExoMet project

Major Collaborative Centres

- CAST CRC (value chain approach)
- Defence Materials Technology Centre (DMTC)
- Centre for Advanced Materials Processing and Manufacturing (AMPAM)
- ARC Centre of Excellence for Design in Light Metals
- ARC Steel Research Hub
- ARC Research Hub for Advanced Manufacturing of Medical Devices
- European ExoMet project on the application of external fields to solidification processes
- Future LiME, Brunel University, London

A Research Thread



- Impetus: Comalco support for my PhD
- **Peritectic solidification: Al-Ti, Cu-Sn**
- Grain refinement: Al alloys with Al-Ti based master alloys, Mg alloys, Ti alloys
- Prediction of grain size: nucleation and grain growth
- **The Interdependence Theory**
- **Application of the research outcomes**

Peritectic Solidification: My Acta Trilogy

Acta Metallurgica, Vol. 25, pp. 77–81. Pergamon Press, 1977. Printed in Great Britain

THE PERITECTIC TRANSFORMATION

D. H. St. JOHN and L. M. HOGAN

Department of Minin

(Rec

Abstract—Some experimen
cussed in relation to tran
between the solid and liq
An approximate diffusion
by diffusion through the e
by direct transformation f
In the Cd–Cd_3Ag system t
mation from the liquid pl

Acta metall. Vol. 35, No. 1, pp. 171–174, 1987 0001-6160/87 $3.00 + 0.00
Printed in Great Britain. All rights reserved Copyright © 1987 Pergamon Journals Ltd

A SIMPLE PREDICTION OF THE RATE OF THE PERITECTIC TRANSFORMATION

D. H. St JOHN and L. M. HOGAN

Department of Mi

Abstract—The rate of a perite
The rate constant is determine
of the phase diagram features
permit easy prediction of rela

Acta metall. mater. Vol. 38, No. 4, pp. 631–636, 1990 0956-7151/90 $3.00 + 0.00
Printed in Great Britain. All rights reserved Copyright © 1990 Pergamon Press plc

THE PERITECTIC REACTION

D. H. StJOHN

CRA Advanced Technical Development, Cannington, W.A. 6107, Australia

(*Received* 27 *July* 1989)

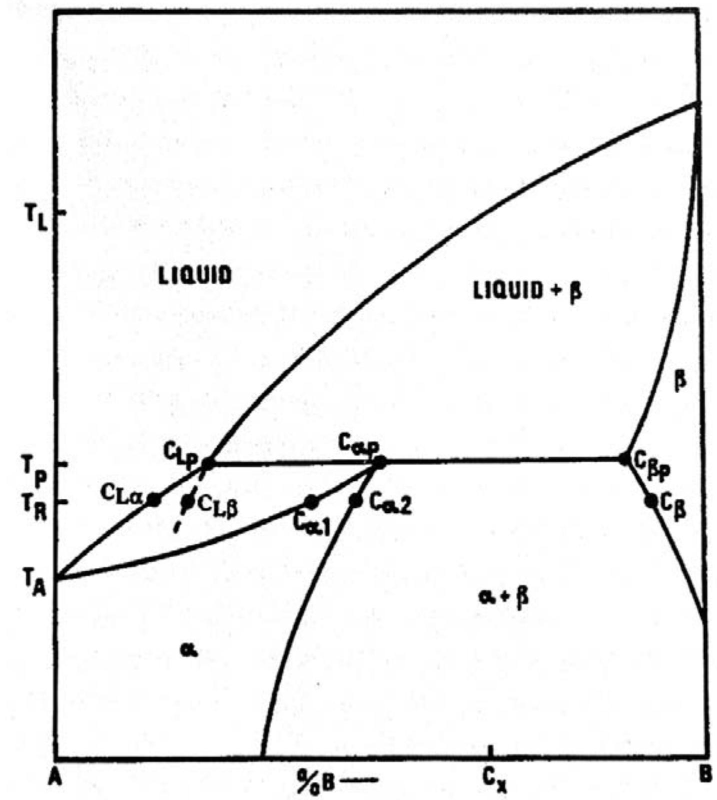
Abstract—Evidence supporting the occurrence of a peritectic reaction prior to the peritectic transformation is re-examined. It is concluded that the peritectic reaction cannot occur at the peritectic temperature for thermodynamic reasons and does not occur in most peritectic systems because crystallization of the peritectic phase occurs directly from the liquid. However, in peritectic systems where the liquidus lines of the pro-peritectic and peritectic phases co-incide a peritectic reaction can occur at temperatures below the peritectic temperature. Evidence is provided by microstructures produced by directional solidification of a Cu–Sn alloy.

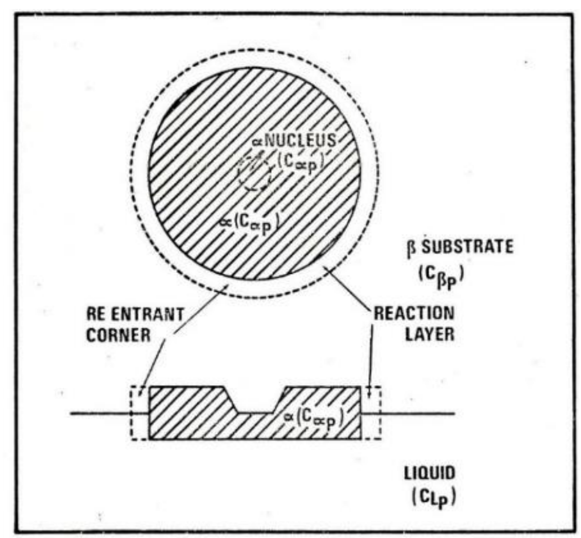
The Peritectic Reaction?

- The classic equilibrium peritectic reaction, β + liquid = α, occurs at a triple point between the three phases at the peritectic temperature

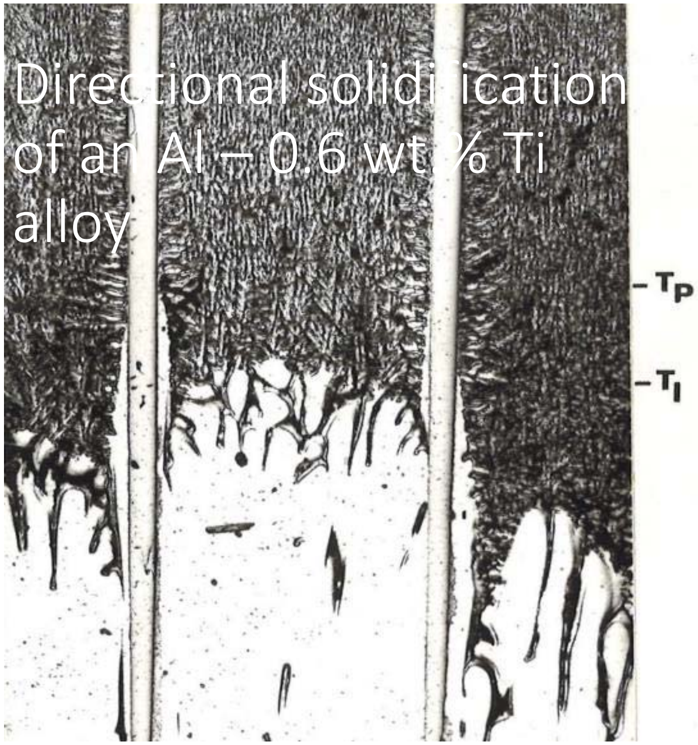
BUT

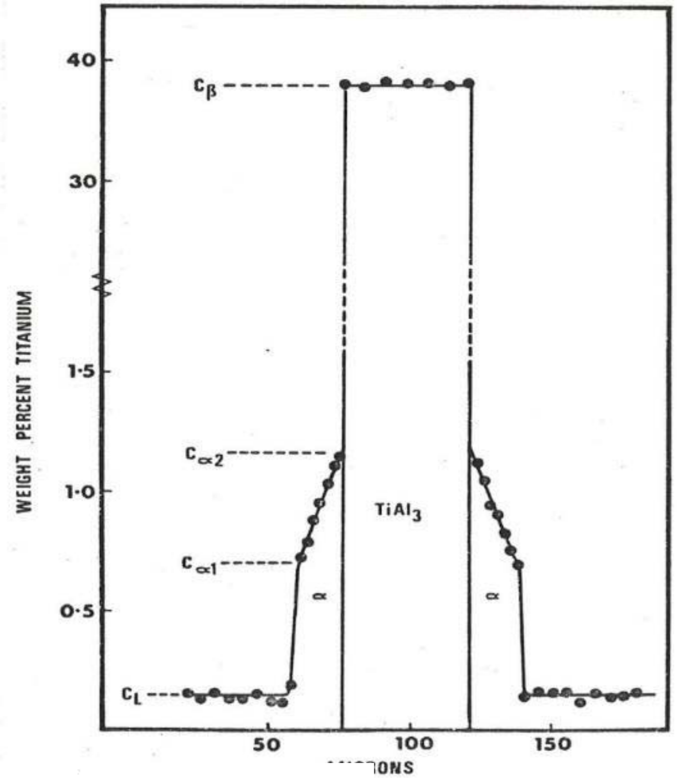
- Direct nucleation and growth of α on β is more likely
- Once α coats β the peritectic transformation can begin
- Independent nucleation of α in the liquid is possible

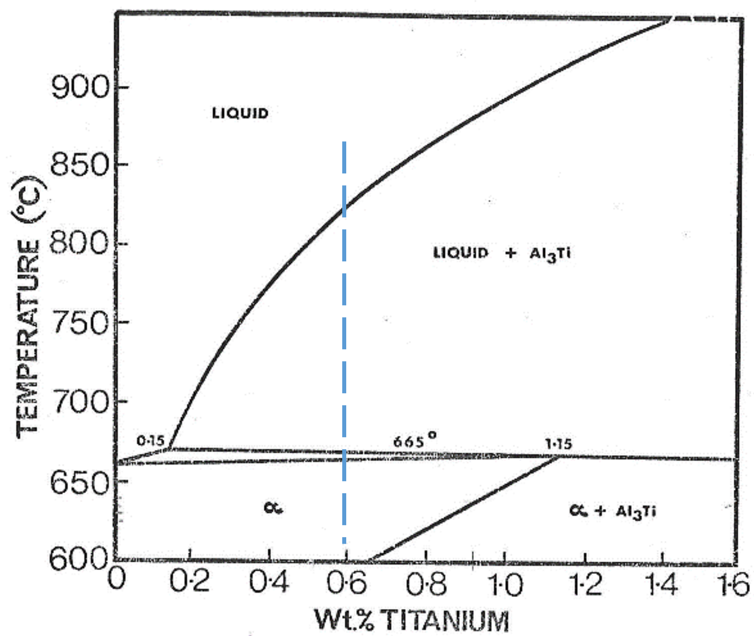




Directional solidification of an Al – 0.6 wt % Ti alloy

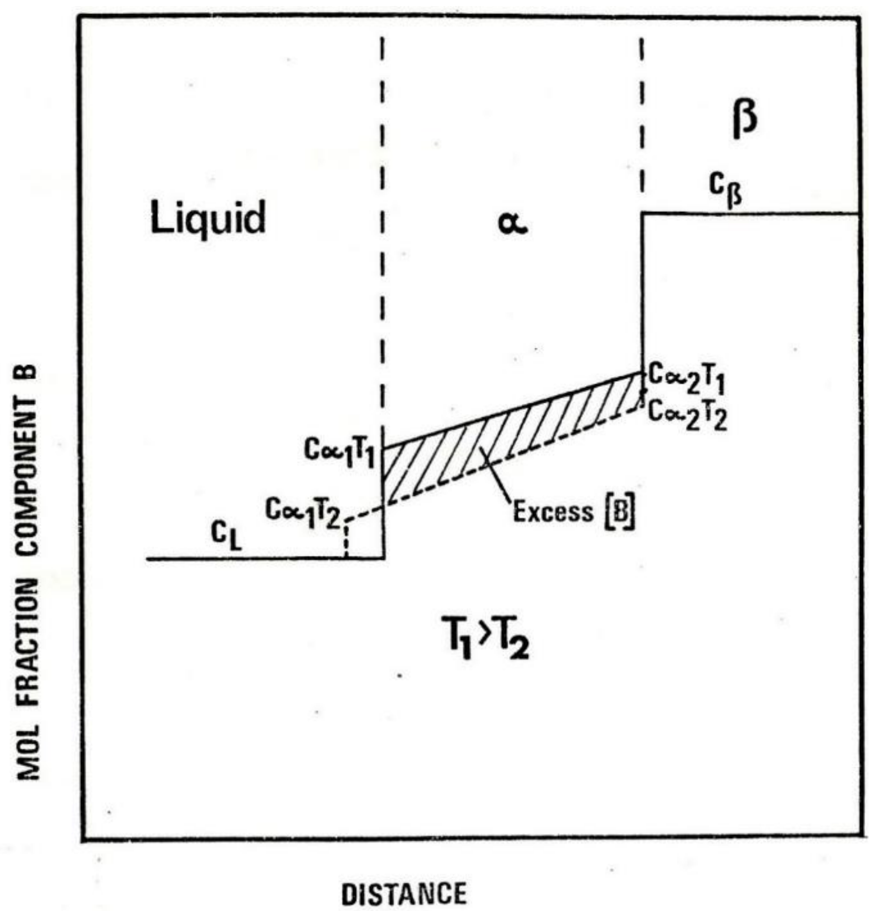






The Peritectic Transformation

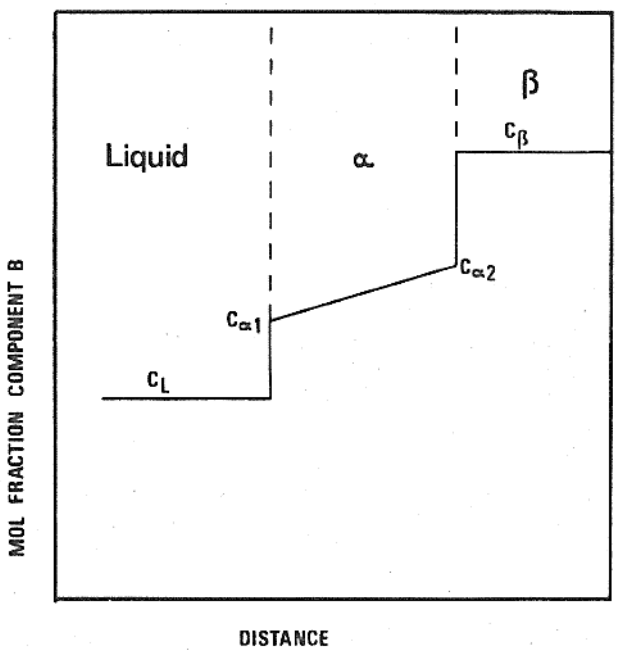
- Rate of peritectic transformation depends on diffusion rate
- Rate increases as undercooling increases due to steeper concentration gradient

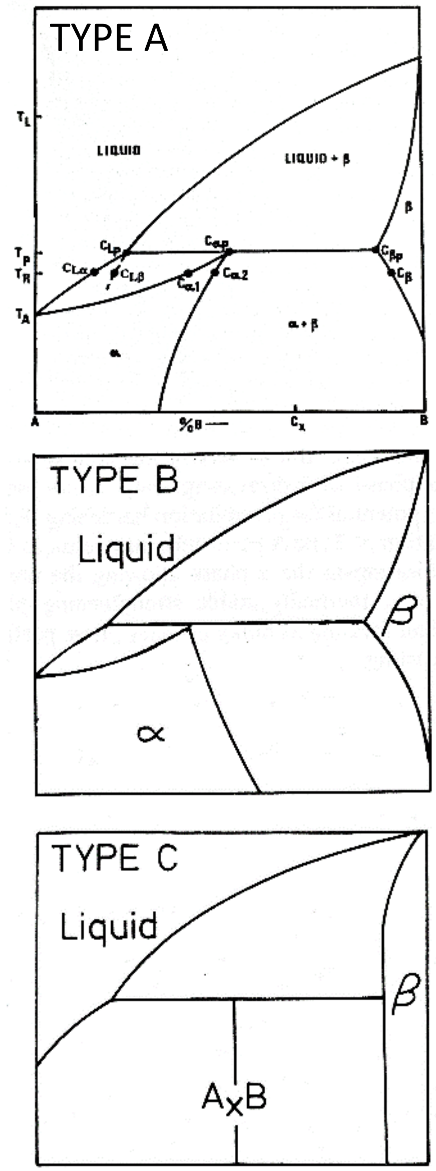


St. John, DH and Hogan, LM, The Peritectic Transformation, *Acta Metallurgica*, 25, 77-81, 1977

Simple predictor of the peritectic transformation

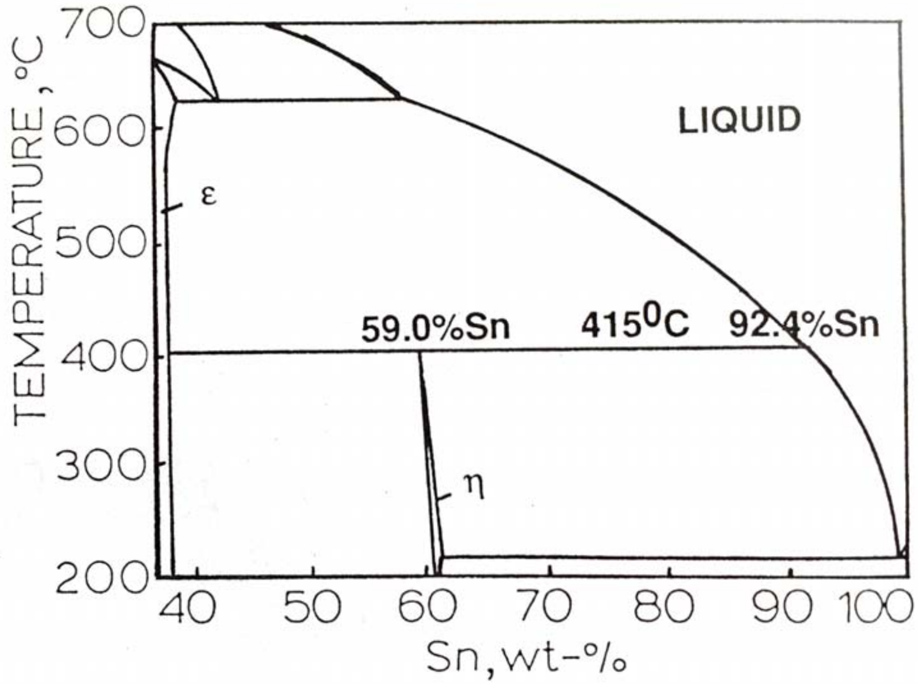
Phase diagram indicates relative rate of transformation

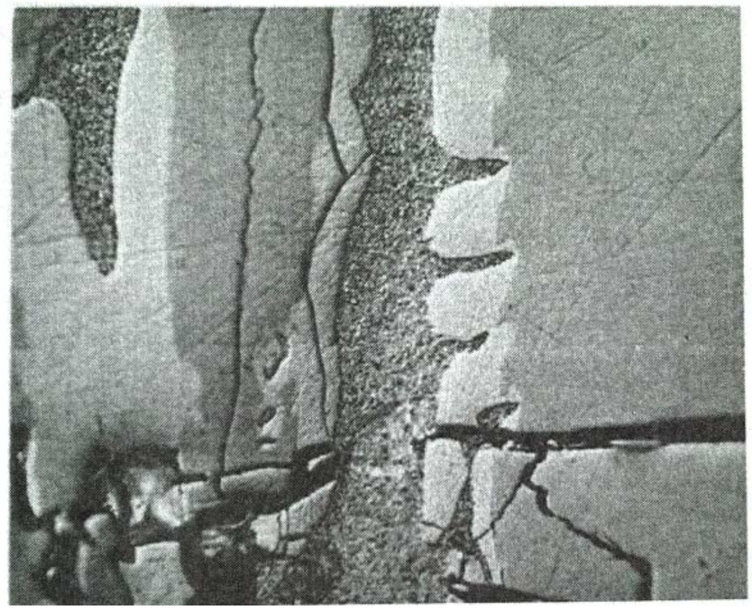


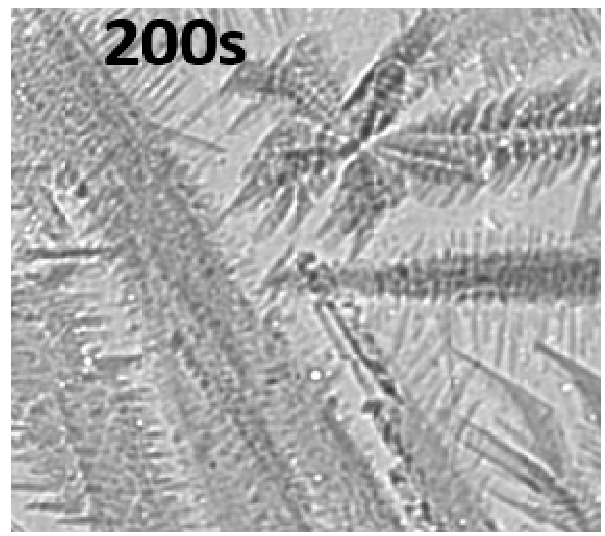


St John, DH and Hogan, LM, A Simple Prediction of the Rate of Peritectic Transformation, *Acta Metallurgica*, 35, 171-174, 1987

Peritectic reaction exists!



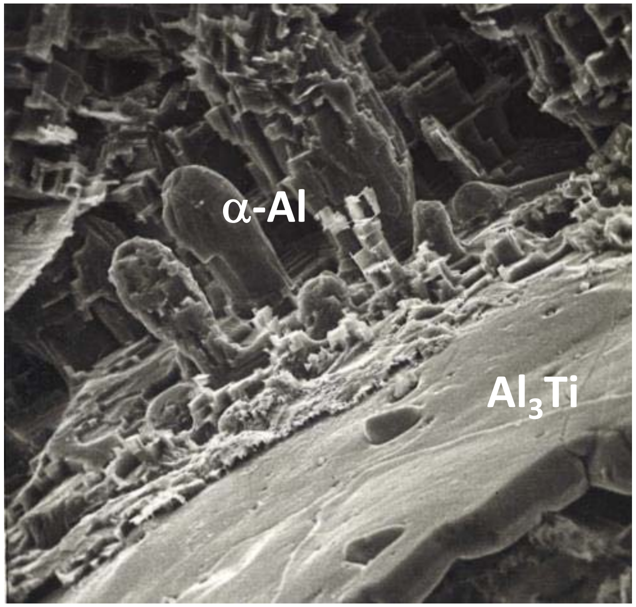


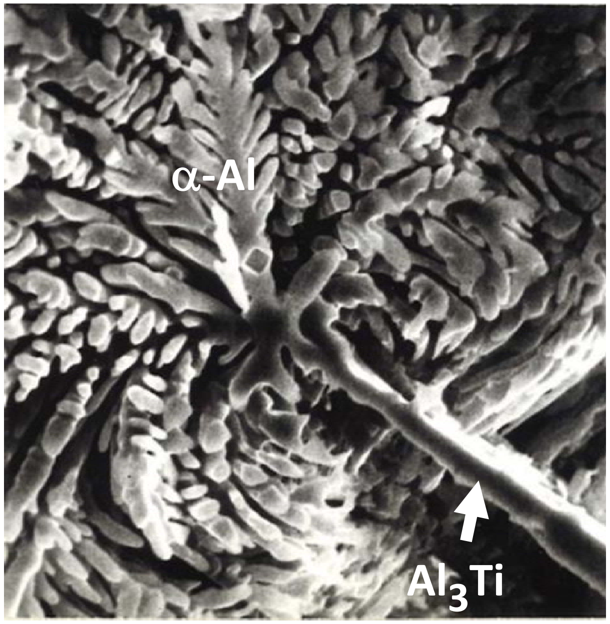


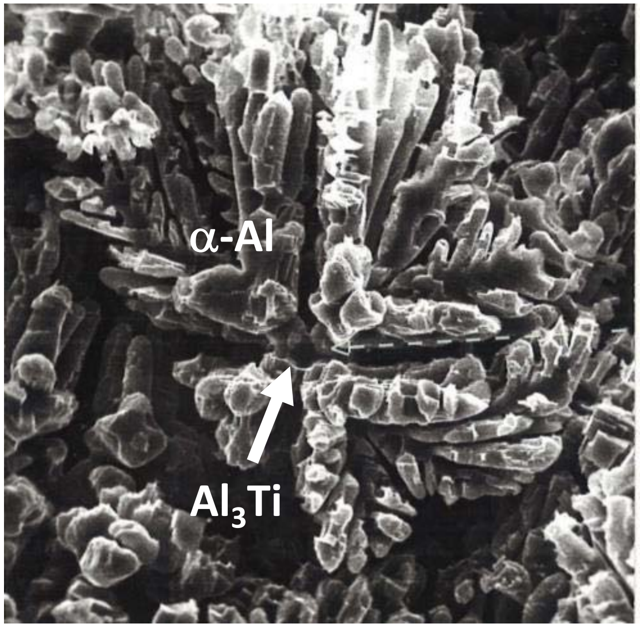
50μm

StJohn, D., The Peritectic Reaction, *Acta Metallurgica*, 38 (4), 631-636, 1990

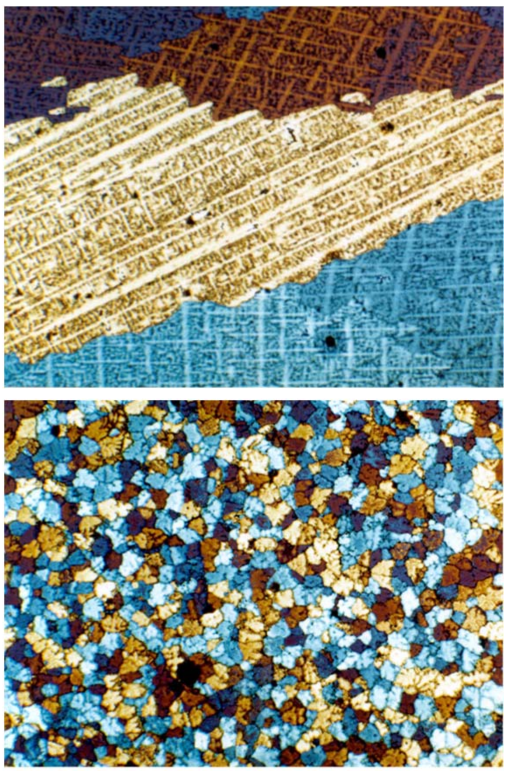
Nucleation & grain refinement





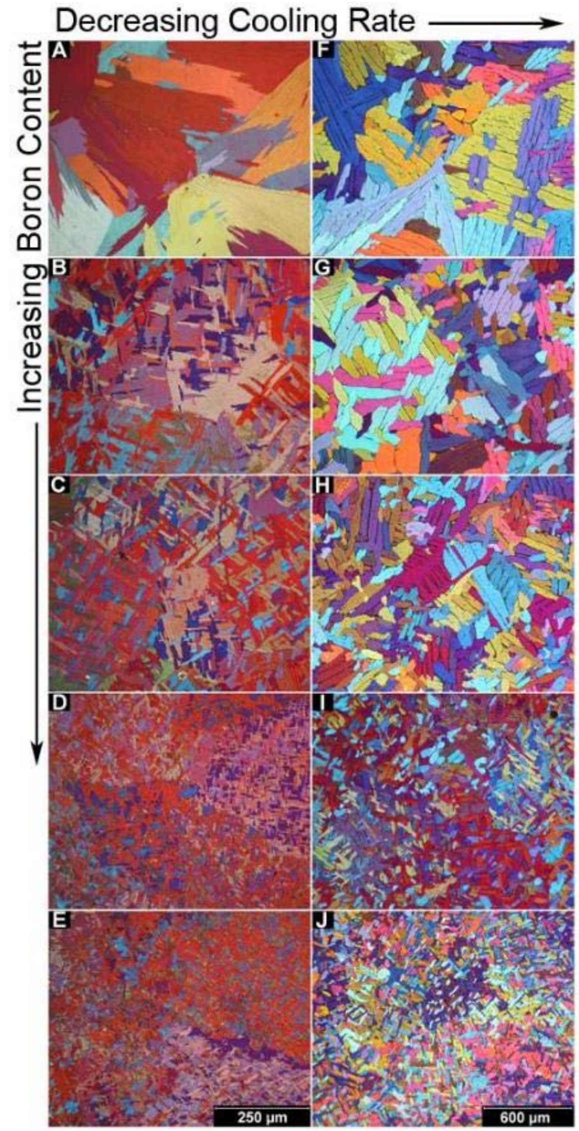


The Interdependence between Constitutional Supercooling (CS) and Nucleation



Al – Ti – TiB_2

Mg - Zr



Ti - B

M.J. Bermingham, S.D. McDonald, K. Nogita, D.H. St. John and M.S. Dargusch, Effects of boron on microstructure in cast titanium alloys, Scripta Materialia 59 (2008) 538–541

ELSEVIER

Available online at www.sciencedirect.com
ScienceDirect

Acta Materialia 59 (2011) 4907–4921

Acta MATERIALIA

www.elsevier.com/locate/actamat

The Interdependence Theory: The relationship between grain formation and nucleant selection

D.H. StJohn [a,*,1], M. Qian [a,1], M.A. Easton [b,1], P. Cao [c,1]

[a] The University of Queensland, St Lucia, Queensland 4072, Australia
[b] Monash University, Clayton, Victoria 3069, Australia
[c] The University of Auckland, Auckland, New Zealand

Received 28 December 2010; received in revised form 12 April 2011; accepted 17 April 2011
Available online 10 May 2011

- Interdependence Theory
- Validation: experimental results, real-time synchrotron x-ray and modelling
- Applied to many alloy systems and casting processes

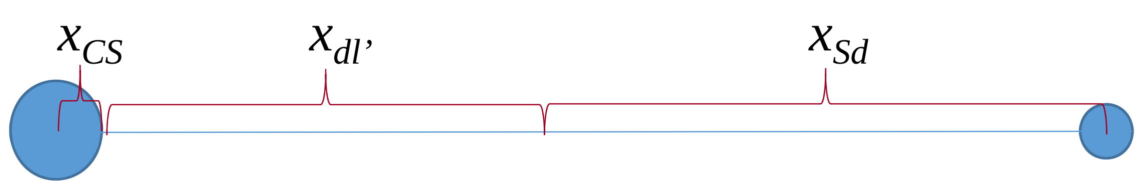
Representing Interdependence

- Both constitutional supercooling and particle characteristics can be represented in terms of temperature
- Three components define the distance between grain centres:

  x_{CS}: growth of previous grain to generate $\Delta T_{CS} = \Delta T_n$

  $x_{dl'}$: length of the diffusion field to where ΔT_n is achieved

  x_{Sd}: distance to next most potent particle



StJohn DH, Qian M, Easton MA, Cao P., The Interdependence Theory: The relationship between grain formation and nucleant selection, Acta Mater., 2011;59: 4907

Role of solute in generating constitutional supercooling

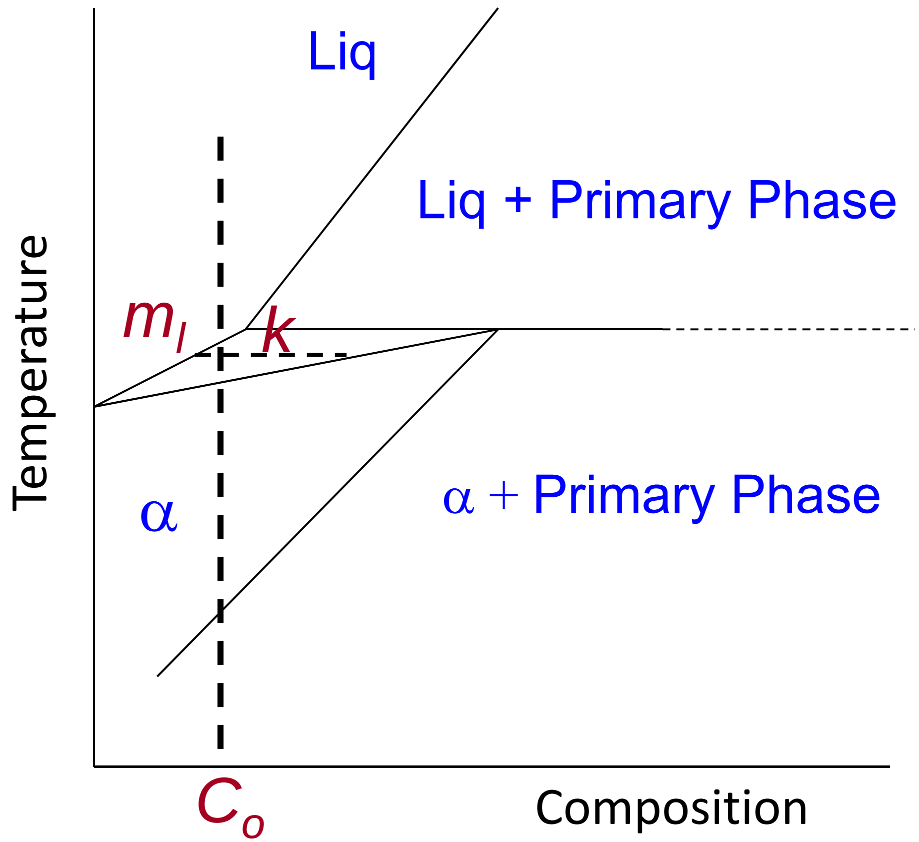
Rate of development of CS is defined by *Q*

Growth

Restriction Factor

$Q = C_o m_l (1-k)$

For complex alloys *Q* can be calculated using a thermodynamic modeling package

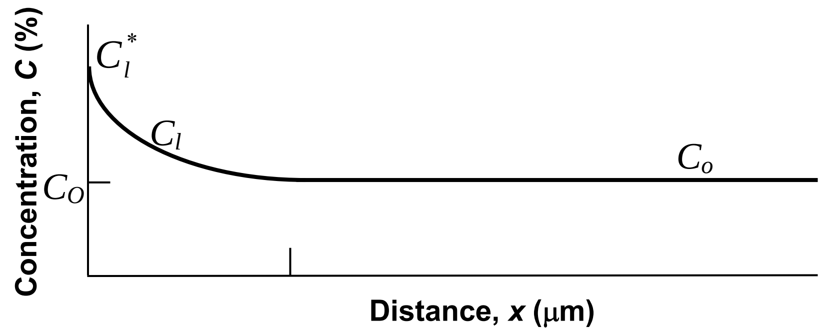


Easton, M. A. and D. H. StJohn, A model of grain refinement incorporating alloy constitution and potency of heterogeneous nucleant particles, Acta Materialia, 2001, 49(10): 1867-1878.

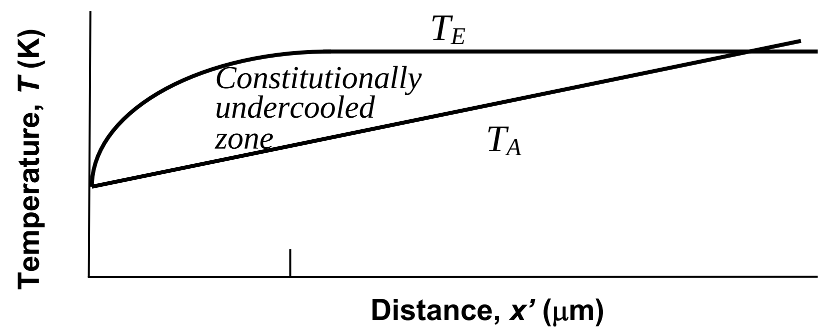
Importance of Q ($=C_o m(k-1)$)

Al Alloys	m(k-1)	Mg alloys	m(k-1)	Ti Alloys	m(k-1)
Ti	**~220**	Fe	52.56	Be	72
Zr	6.8	**Zr**	**38.29**	**B**	**66**
Si	5.9	Ca	11.94	Si	21.7
Cr	3.5	Si	9.25	Ni	14.3
Ni	3.3	Zn	5.31	O	10.2
Mg	3.0	Cu	5.28	Co	8.8
Fe	2.9	Al	4.32	Y	7.9
Cu	2.8	Sr	3.51	Sc	6.7
Mn	0.1	Ce	2.74	Cu	6.5
		Y	1.70	**Al**	**~ 0**
		Mn	0.15	**V**	**~ 0**

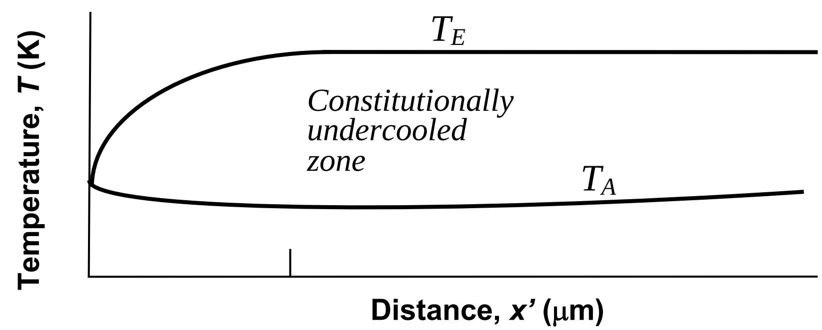
Constitutional Supercooling (CS)



Solute rejection at the solid-liquid interface



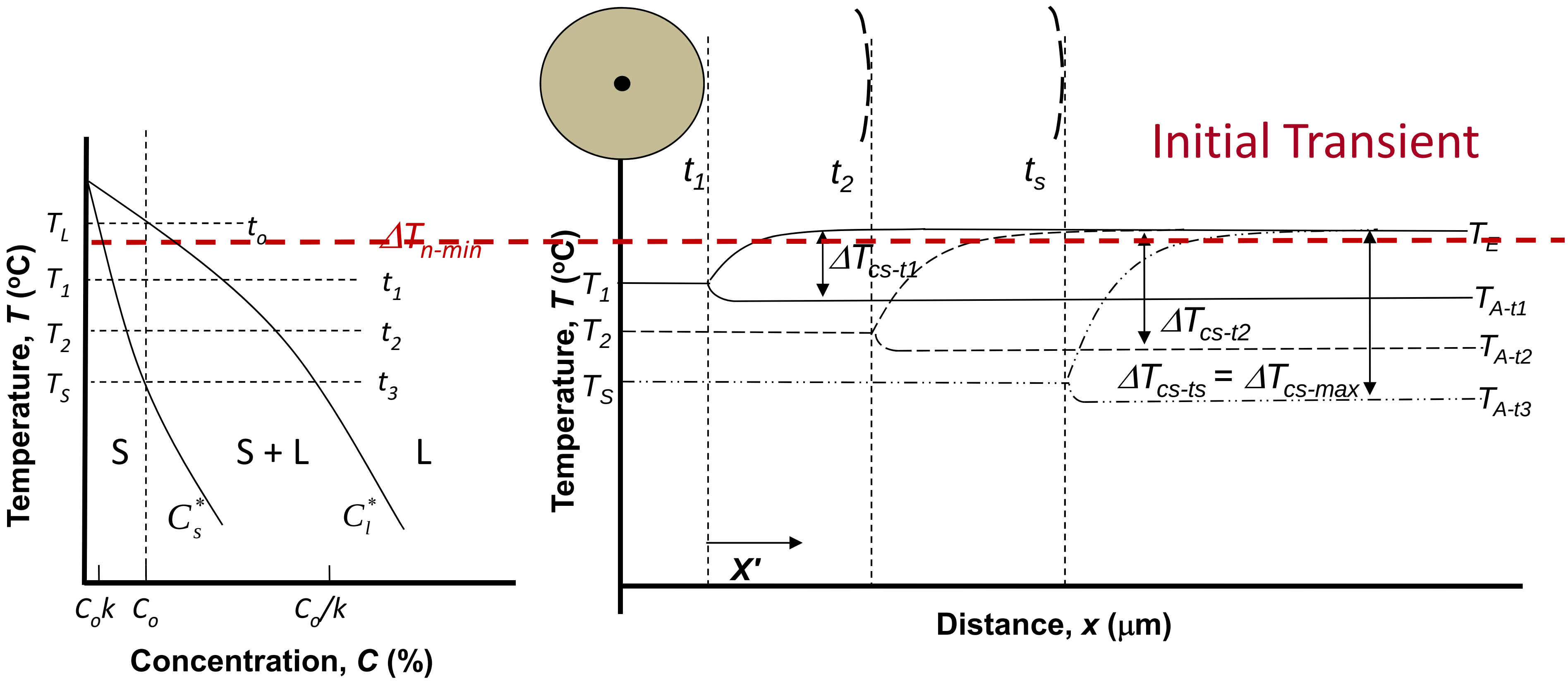
Directional solidification



Equiaxed solidification

Ian Polmear, David StJohn, Jian-Feng Nie, Ma Qian, Light Alloys, (5th Edition) 2017

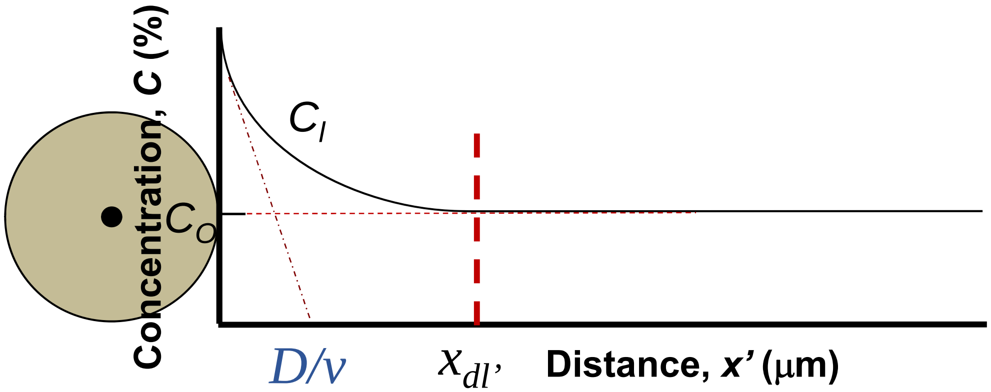
Development of *CS* zone and x_{CS}



$$x_{CS} = \frac{D \cdot \Delta T_{n-min}}{vQ}$$

Qian, M., P. Cao, M.A. Easton, S.D. McDonald, D.H. StJohn, An analytical model for constitutional supercooling-driven grain formation and grain size prediction, (2010) Acta Materialia, 2010;58: 3262

Diffusion Length, $x_{dl'}$



$$C_l(x') = (C_l^*(x) - C_0)\exp(-\frac{v}{D}\cdot x') + C_0$$

$$l_d = D/v$$

Tiller WA, Jackson KA, Rutter JW, Chalmers B. Acta Metall. 1953;1:428.
Smith VG, Tiller WA, Rutter JW. Can. J. Physics 1955;33:723

But for the initial transient

$$l_D = \frac{D}{v}\cdot\left(\frac{C_l^* - C_0}{C_l^*\cdot(1-k)}\right)$$

Trivedi R, Kurz W. Acta Mater. 1994;42:15

$$C_l(x') = (C_l^* - C_0)\exp\left[-\frac{v}{D}\cdot\left(\frac{C_l^*\cdot(1-k)}{C_l^* - C_0}\right)x'\right] + C_0$$

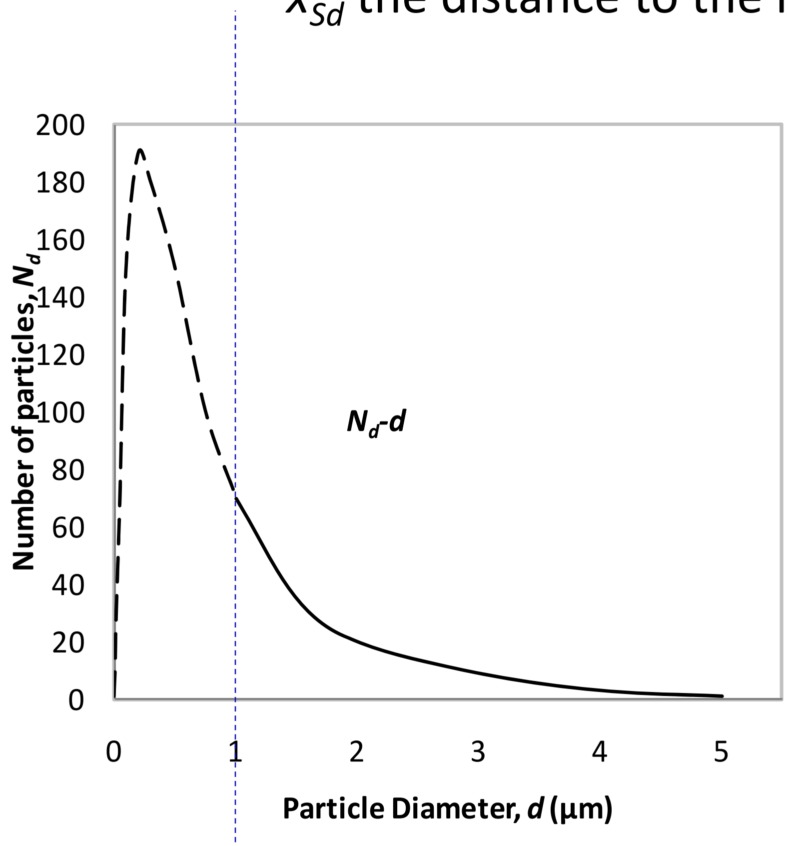
$$x_{dl'} = \frac{4.6D}{v}\cdot\left(\frac{C_l^* - C_0}{C_l^*\cdot(1-k)}\right)$$

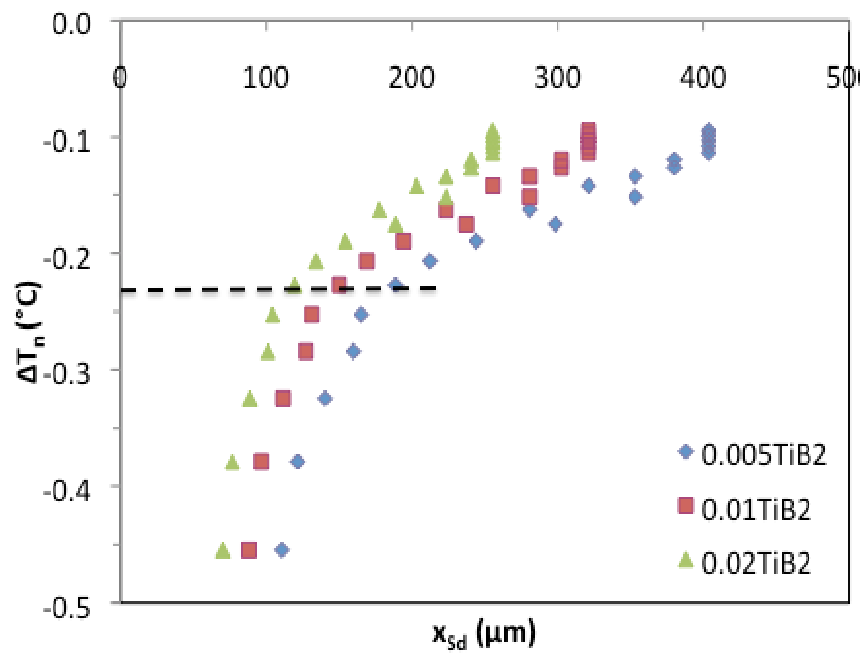
StJohn DH, Qian M, Easton MA, Cao P., The Interdependence Theory: The relationship between grain formation and nucleant selection, Acta Mater., 2011;59: 4907

Particle characteristics: nucleation potency and distribution

Particle Characteristics (ΔT_n) and x_{Sd}

x_{Sd} the distance to the next most potent particle





Based on TiB_2 size data present in Al5Ti1B master alloys

$\Delta T_n = 4\sigma/(\Delta S_v d)$ $S_d = 100\mu m/N_d$

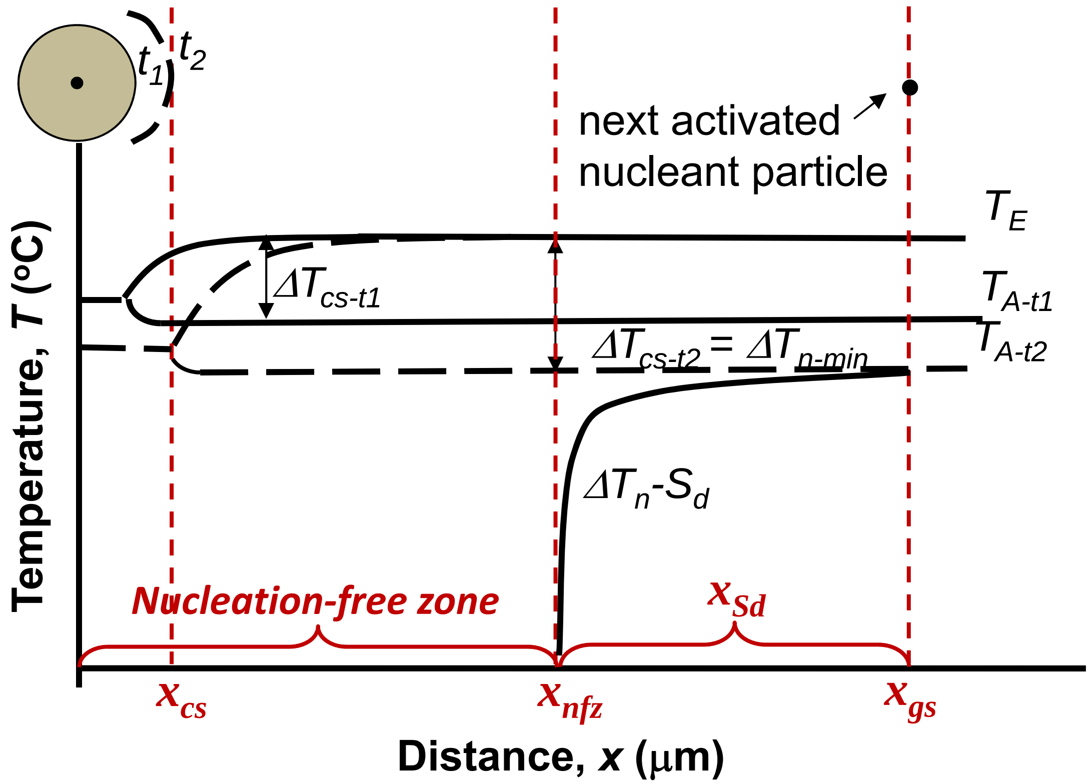
σ - solid-liquid interfacial energy

ΔS_v - entropy of fusion

Greer AL, Bunn AM, Tronche A, Evans PV, Bristow DJ. Acta Mater. 2000;48:2823.

Interaction between Constitutional Supercooling and Nucleation

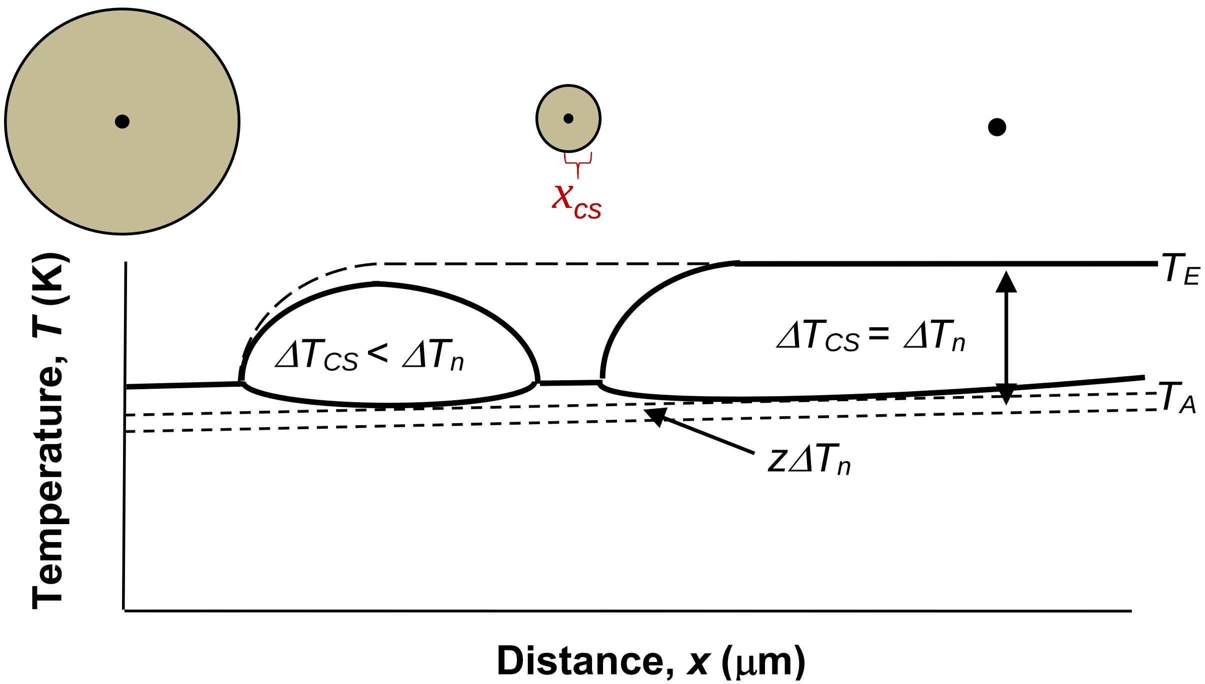
Nucleation occurs at the intersection of T_A and ΔT_n-S_d at time t_2



The Interdependence Theory

StJohn DH, Qian M, Easton MA, Cao P., The Interdependence Theory: The relationship between grain formation and nucleant selection, Acta Mater., 2011;59: 4907

Repeated nucleation only requires a fraction, z, of $\Delta T_{n\text{-}min}$ to be generated



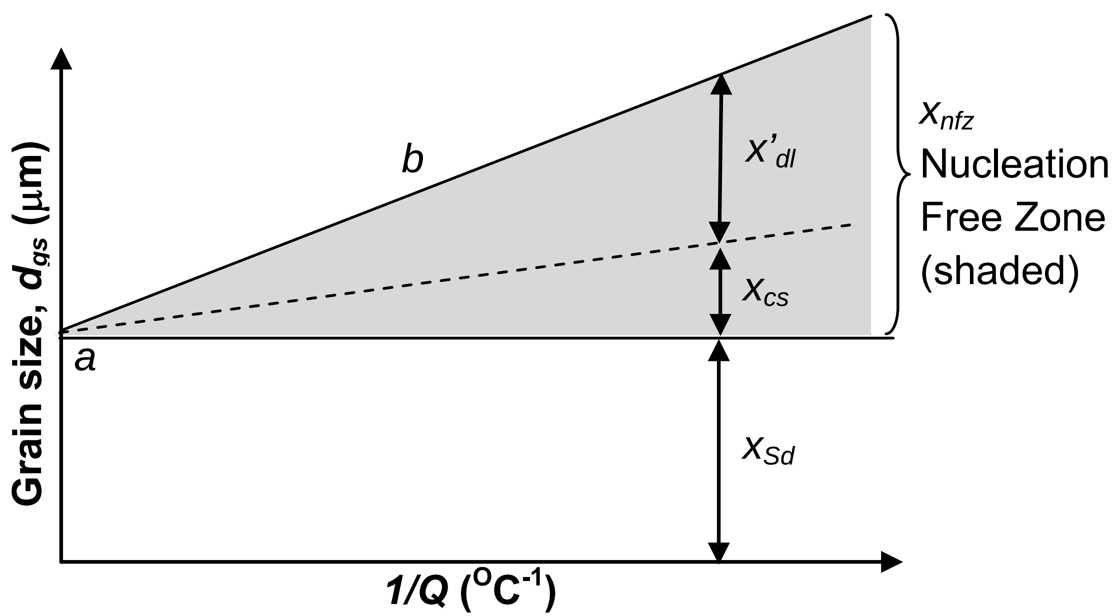
$$x_{cs} = \frac{D \cdot z\Delta T_{n-min}}{vQ}$$

StJohn DH, Qian M, Easton MA, Cao P., The Interdependence Theory: The relationship between grain formation and nucleant selection, Acta Mater., 2011;59: 4907

The Interdependence equation

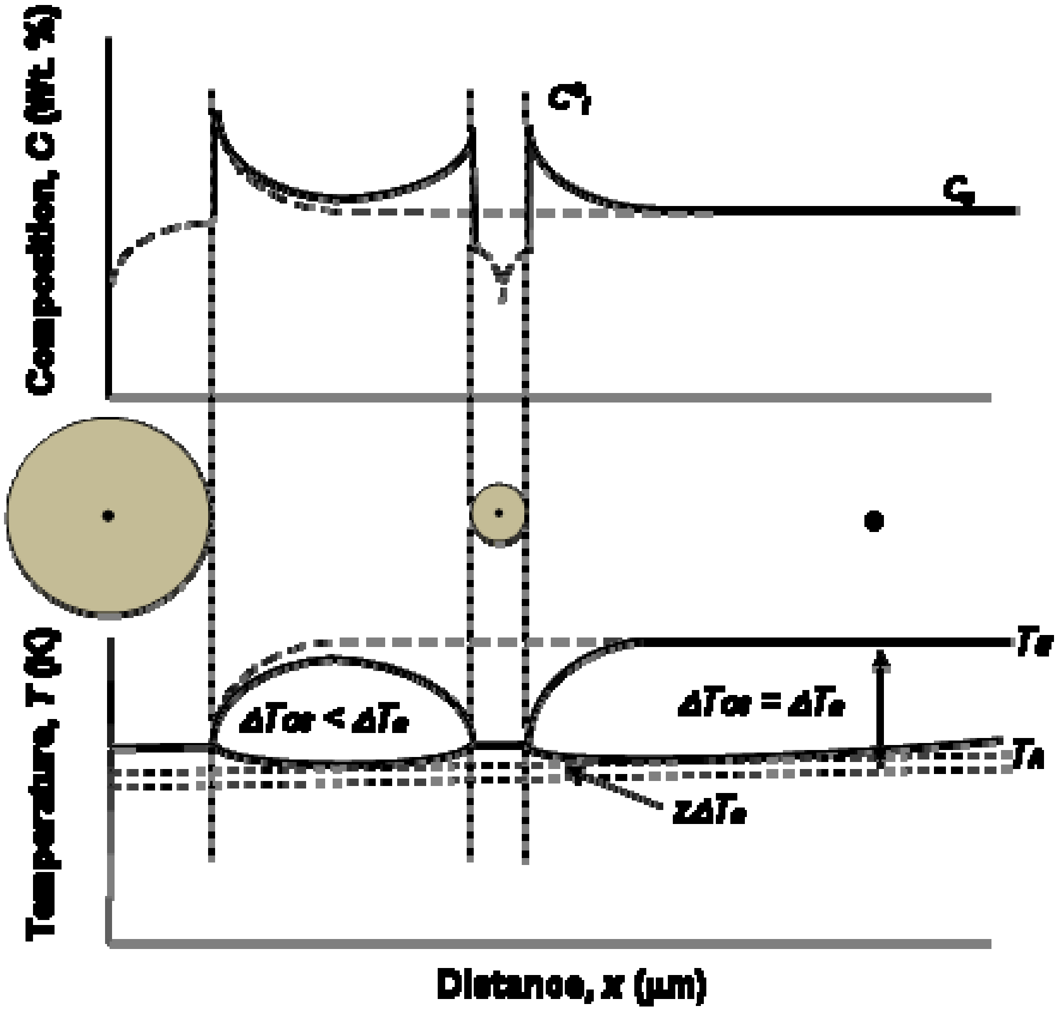
$$d_{gs} = \frac{D \cdot z\Delta T_{n-min}}{vQ} + \frac{4.6D}{v} \cdot \left(\frac{C_l^* - C_0}{C_l^* \cdot (1-k)} \right) + x_{Sd}$$

$$d_{gs} = x_{cs} + x'_{dl} + x_{Sd}$$



StJohn DH, Qian M, Easton MA, Cao P., The Interdependence Theory: The relationship between grain formation and nucleant selection, Acta Mater., 2011;59: 4907

Solute Accumulation

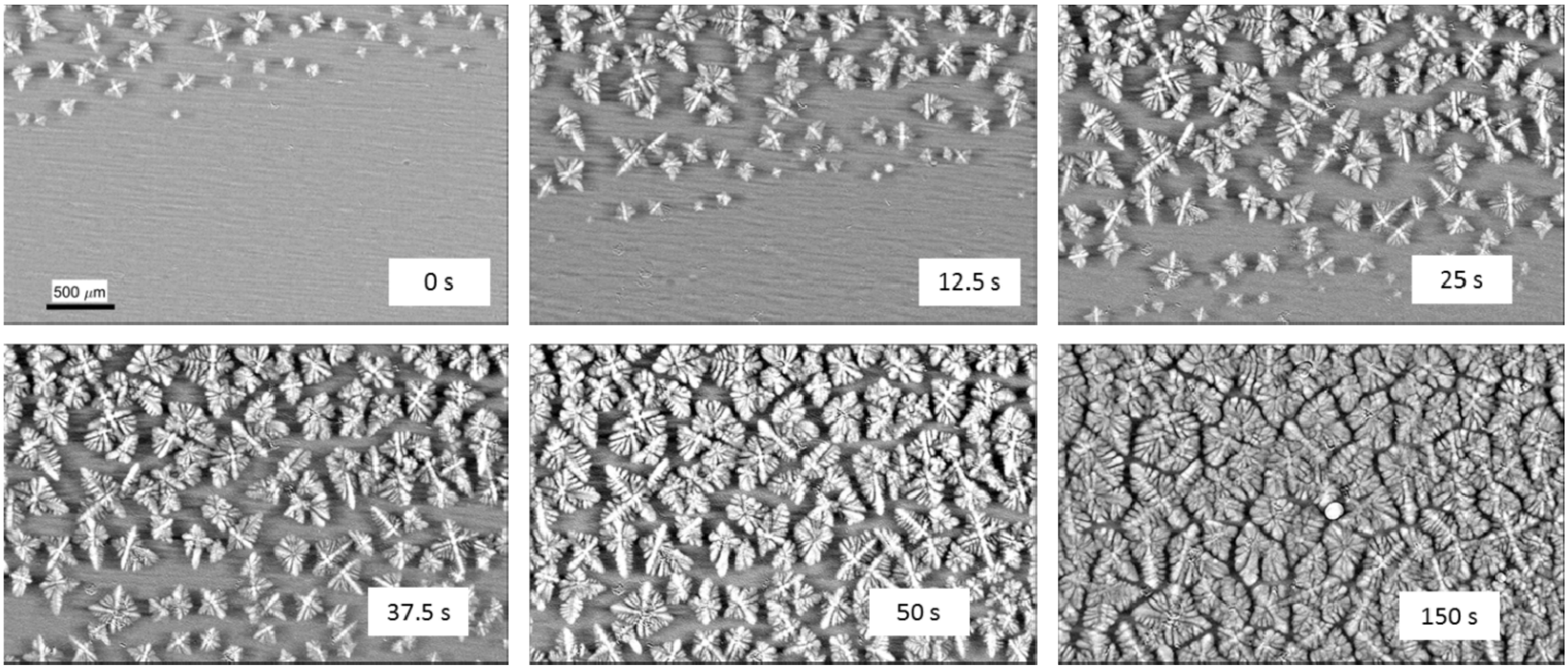


StJohn, D.H., Prasad A., Easton M.A., Qian M., The Contribution of Constitutional Supercooling to Nucleation and Grain Formation, Metallurgical and Materials Transactions A: Volume 46, Issue 11 (2015), 4868-4885

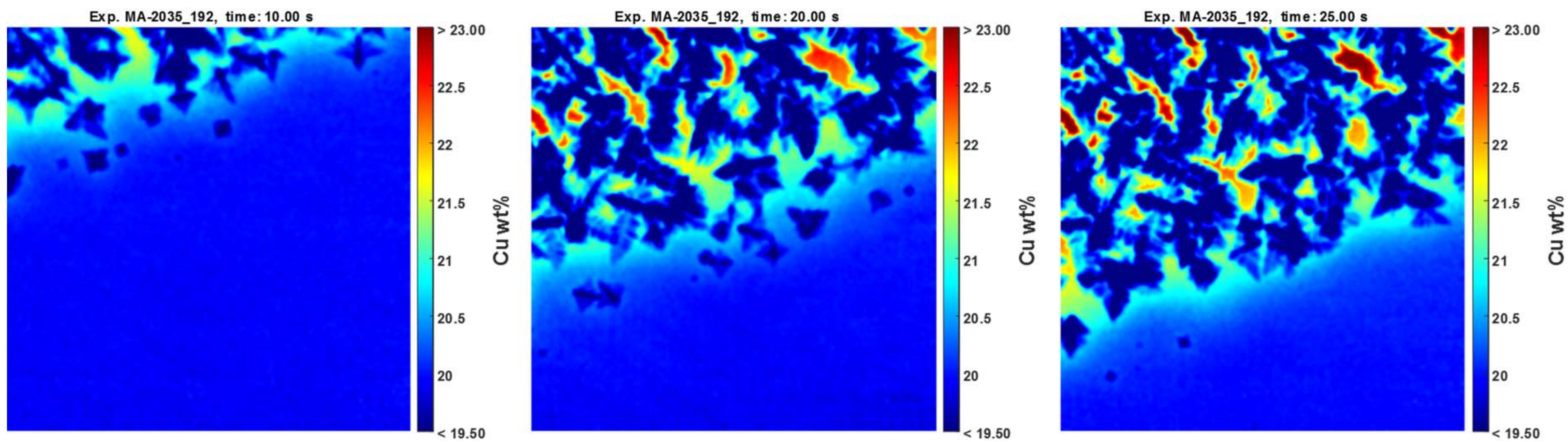
What does the model imply?

- Wave-like nucleation
- Waves of nucleation separated by a nucleation-free zone and the spacing of potent nucleant particles
- In a well grain refined alloy no further nucleation events occur after the initial wave of nucleation occurs

Al – 15% Cu from real-time synchrotron x-ray study



Prasad, E Liotti, SD McDonald, K Nogita, H Yasuda, PS Grant and DH StJohn, Real-time synchrotron x-ray observations of equiaxed solidification of aluminium alloys and implications for modelling, *Mater. Sci. and Eng*. 84 (2015) 012014 doi:10.1088/1757-899X/84/1/012014



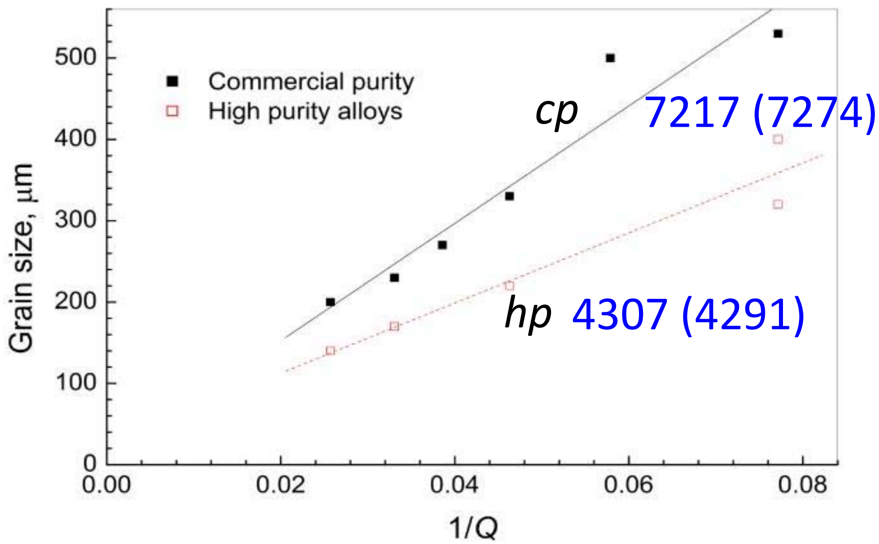
Real-time X-ray Synchrotron images of an Al-20% Cu alloy.

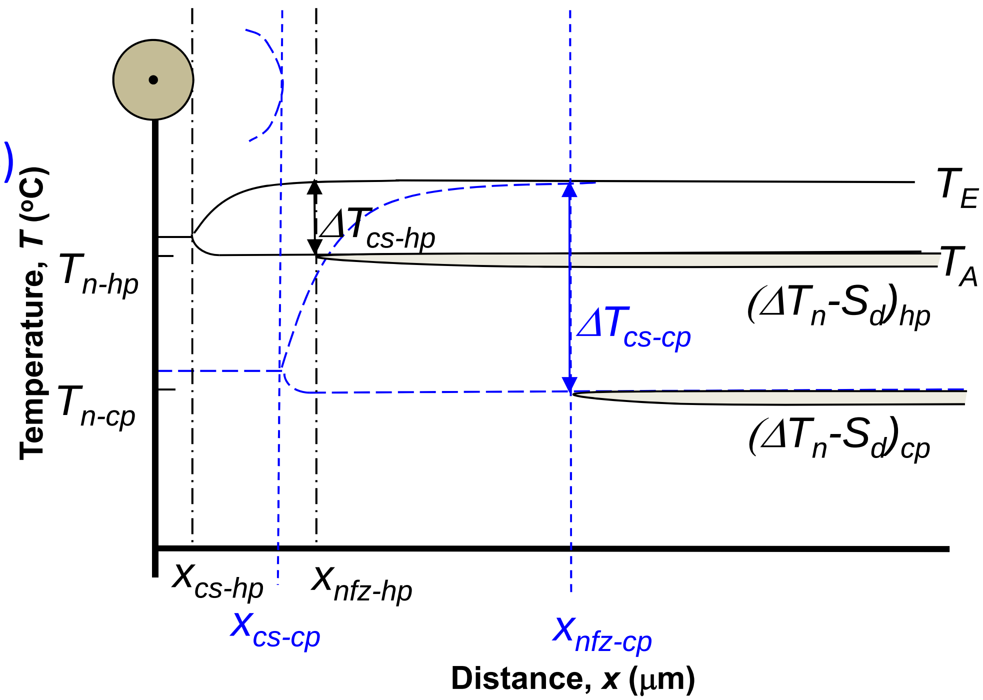
The colours represent differences in composition.

It is possible to measure concentration profiles in the solid and liquid phases, the point of nucleation, and growth rate of the grain-liquid interface. From these measures the diffusion rate of Cu in the liquid Al, the amount of constitutional supercooling generated, the nucleation undercooling and growth velocity can be calculated.

Courtesy of Enzo Liotti and Patrick Grant,
Oxford University

Mg – Al alloys





Commercial purity to high purity

- the slope decreases, thus $\Delta T_{n\text{-}min}$ decreases
- the intercept is unchanged and very small, thus $d_{gs} = x_{nfz}$

StJohn DH, Qian M, Easton MA, Cao P., The Interdependence Theory: The relationship between grain formation and nucleant selection, Acta Mater., 2011;59: 4907

How has the knowledge been used?

- Peritectic solidification
  - Steel research in Japan
  - Superconducting ceramics
  - Pb-free solders (Nihon Superior)
  - Intermetallic transformations
- Grain refinement and Q
  - Cost reduction and problem solving (Comalco, Tomago)
  - Patented Zr master alloy (Magontec)
  - Incorporated into Magma casting design software
- Interdependence model
  - Understanding mechanisms responsible for refinement
  - Applies broadly to all alloys and casting conditions

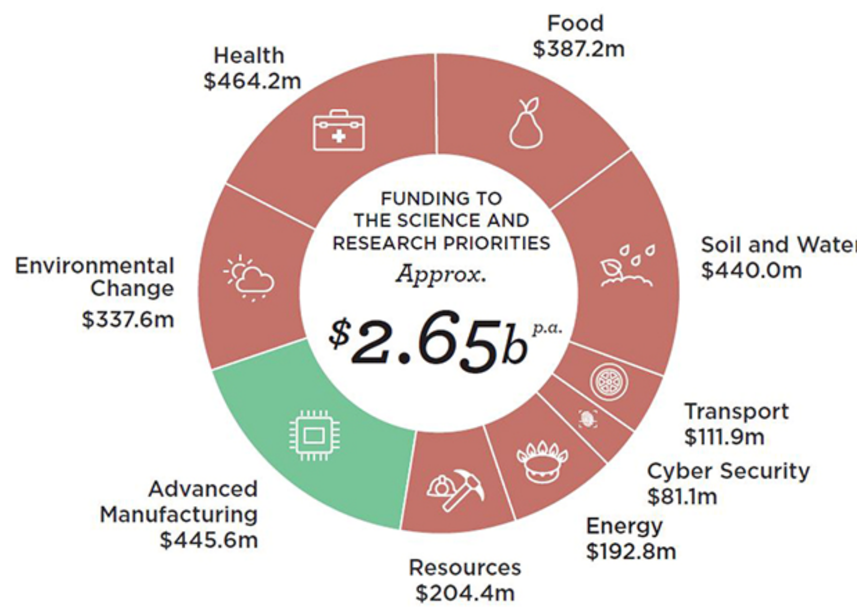
The people who make it happen

- Industry: technology champions
- Government: policy makers, public servants and facilitation of funding opportunities, setting research priorities
- Research collaborators, PhD students and Postdocs
- University administrators and support mechanisms
- Know what’s going on to capture opportunities

Opportunities

- Changing assessment criteria
- Measuring impact
- Industry engagement
- Collaboration across areas of expertise and capability

Australian Government Expenditure on Science and Research Priorities



http://www.science.gov.au/scienceGov/ScienceAndResearchPriorities/Pages/Advanced-manufacturing.aspx

- Strategically aligning Australia's research focus with its strengths in manufacturing
- Strengthening engagement between research and industry (particularly small to medium-sized enterprises)
- Scaling-up existing activities that add value to Australian manufactured products
- Improving Australia's capability in cyber-physical systems interfaces

Advanced Engineering Building, The University of Queensland

Plenary: Professor D. StJohn, University of Queensland, Australia