

Microstructural  
Kinetics  
Group



UNIVERSITY OF  
CAMBRIDGE

Department of Materials Science and Metallurgy

# Grain Refinement of Aluminium:

— an example of nucleation control

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## Acknowledgements

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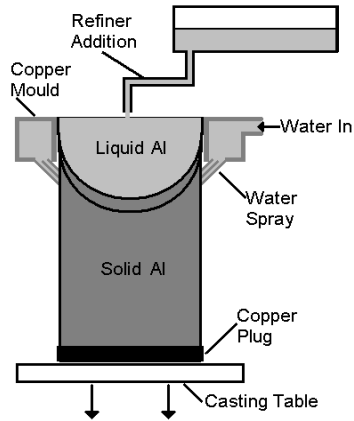
M. Vandyoussefi

EPSRC (UK)

### *Industrial Collaborators —*

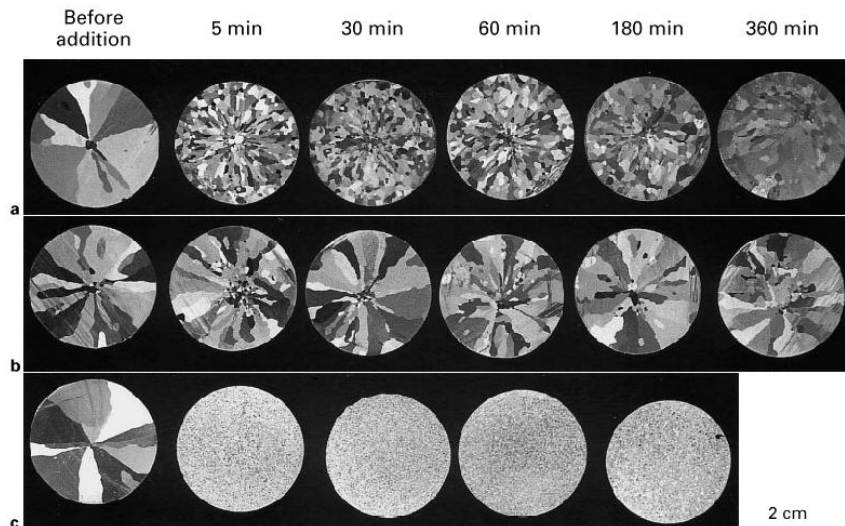
- Alcan Inc.
- London and Scandinavian Metallurgical Co Ltd
- Pechiney

## DC Casting of Aluminium



Annual production of Al:  
 $23 \times 10^6$  tonnes  
 at \$1370 per tonne  
 gives annual value of \$31 billion

Inoculation gives a uniform structure of fine equiaxed grains, shown here in TP-1 grain-refining test samples



[Vandyoussefi, Worth & Greer, *Mater. Sci. Technol.*, **16** (2000) 1121.]

## Typical Grain Refiners for Aluminium and its Alloys

Most commonly used refiners are based on Al-Ti-B, for example:

### **Al-5Ti-1B (wt%)**

- Al-5Ti-0.2B, Al-3Ti-1B and Al-3Ti-0.2B are also used
- have  $\text{TiB}_2$  and  $\text{Al}_3\text{Ti}$  particles in an aluminium matrix

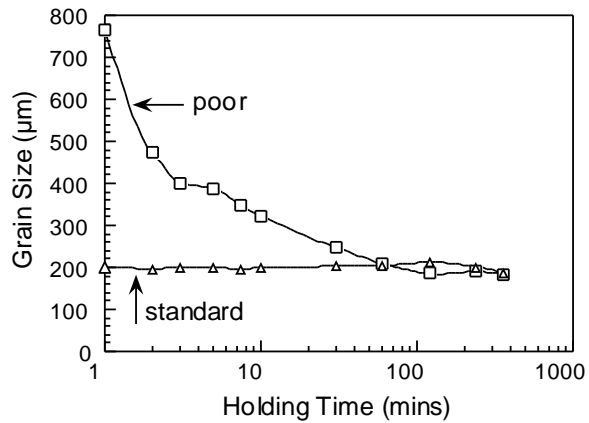
There is increasing interest in Al-Ti-C refiners, for example:

### **Al-3Ti-0.15C (wt%)**

- have  $\text{TiC}$  and  $\text{Al}_3\text{Ti}$  particles in an aluminium matrix

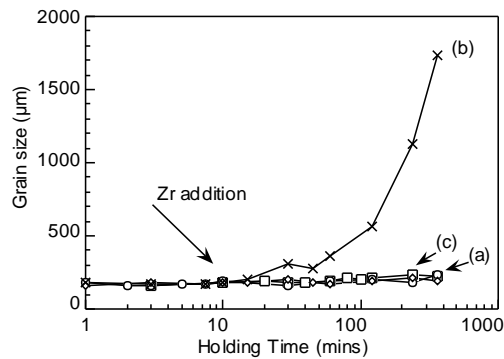
## Issues in Grain Refinement

- **which refiner** to choose?
- **how much** to add? (what is the minimum addition level to suppress columnar growth?)
- how to **predict** grain size as a function of:
  - refiner addition level
  - cooling rate
  - solute content of the melt?
- causes of **variability** in performance?
- how to avoid **poisoning** by particular solutes in the melt?
- why are refiners so **inefficient**? —  $\leq 1\%$  of particles initiate grains



The performance of a 'poor' batch of refiner can improve on holding in a melt of commercial-purity aluminium. (1 ppt addition of two different batches of Al-5Ti-1B, held in a stirred melt at 760°C.)

[A.M. Bunn, Ph.D. Thesis (1998), University of Cambridge]

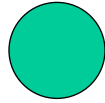


- (a) the performance of a 'good' refiner does not fade
- (b) addition of Zr causes progressive poisoning
- (c) a Ta-treated refiner appears immune to the poisoning

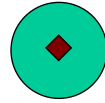
[A.M. Bunn, Ph.D. Thesis (1998), University of Cambridge]

## Nucleation events

— are the starting point for growth of a new phase



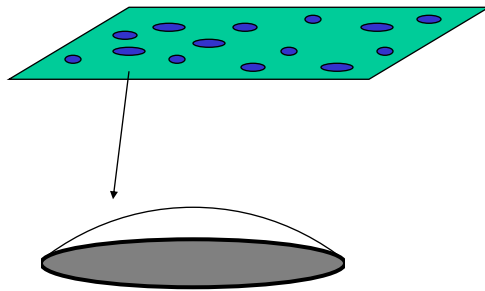
homogeneous



heterogeneous

## Heterogeneous nucleation

— formation of spherical-cap nuclei on a planar substrate



## Importance of Nucleation

### Materials Processing

- control of grain size in metal casting
- control of transparency in polymers
- .....

### Environmental

- clouds and precipitation
- frost damage to plants

### Medical

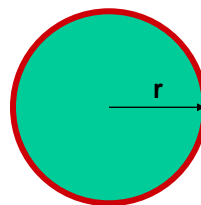
- prions and CJD
- kidney stones

## Work of formation of cluster of new phase

generate **volume** of new phase  
and **interface** between old and  
new phases

$\Delta G_V$  free energy change per  $m^3$

$\sigma$  interfacial energy per  $m^2$



In the **classical theory of nucleation**, the work of cluster formation is:

$$W = \frac{4}{3} \pi r^3 \Delta G_V + 4 \pi r^2 \sigma$$

## Thermodynamics

- use of macroscopic  $\Delta G_v$  and  $\sigma$  in the classical model?
- diffuse interface theory
- density functional approaches
- ab-initio calculations

## Kinetics

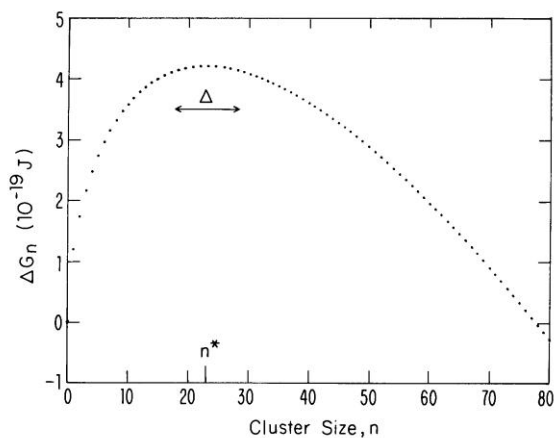
- classical assumption of bimolecular reactions
- transient phenomena — not just steady state
- model complex processing sequences

## Thermodynamics

— work of cluster formation, shows a maximum

in the critical region  $\Delta$ ,  
there is essentially a 1-D  
random diffusion in size

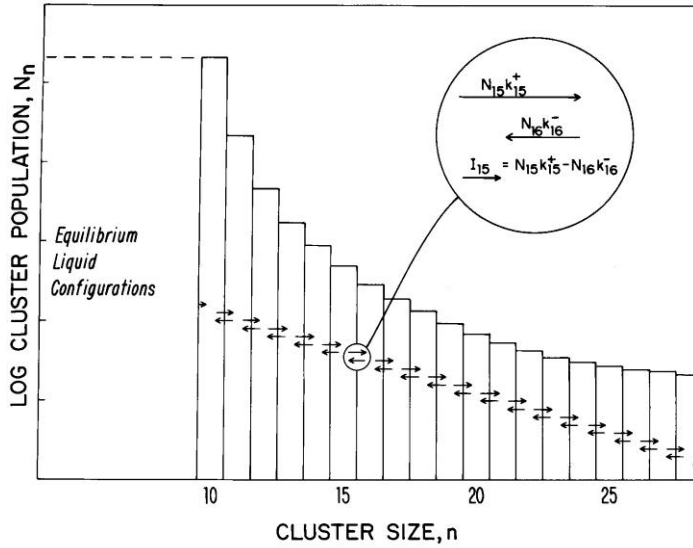
In region  $\Delta$ ,  $W$  is within  $kT$   
of  $W^*$



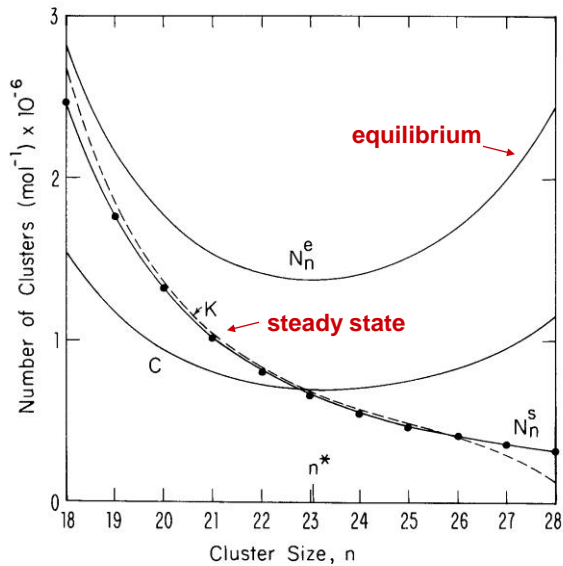
Calculation for homogeneous crystal nucleation in  
lithium disilicate glass

## Cluster dynamics

— a cluster size distribution is built up through a series of reactions

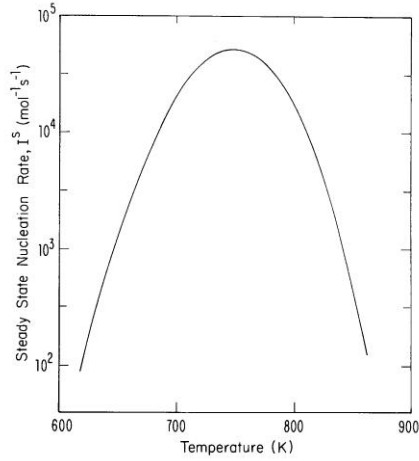


Cluster size distribution near the critical size —



## Steady state nucleation rate

— can be well approximated analytically

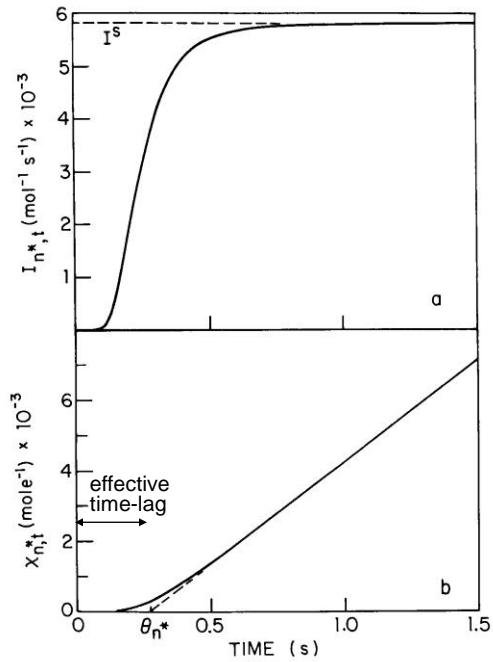


**Input parameters** —  $\Delta G_V$   
 $\sigma$   
viscosity — all temperature-dependent

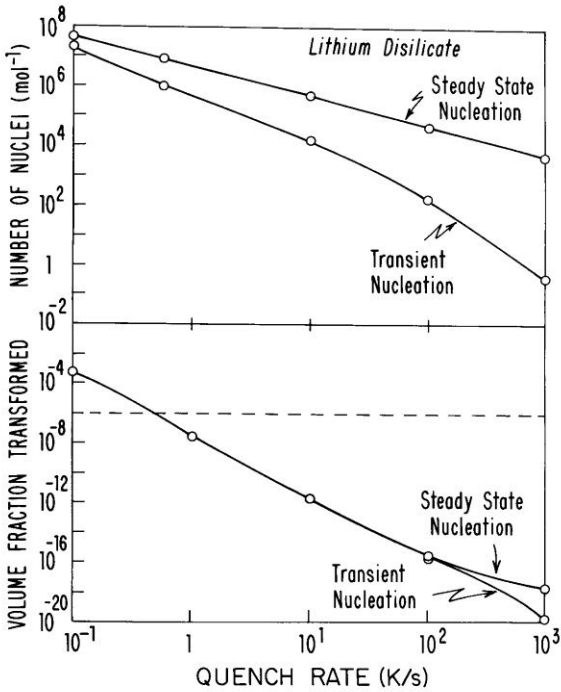
## Transient effects

**Nucleation rate** —

**Number of nuclei** —

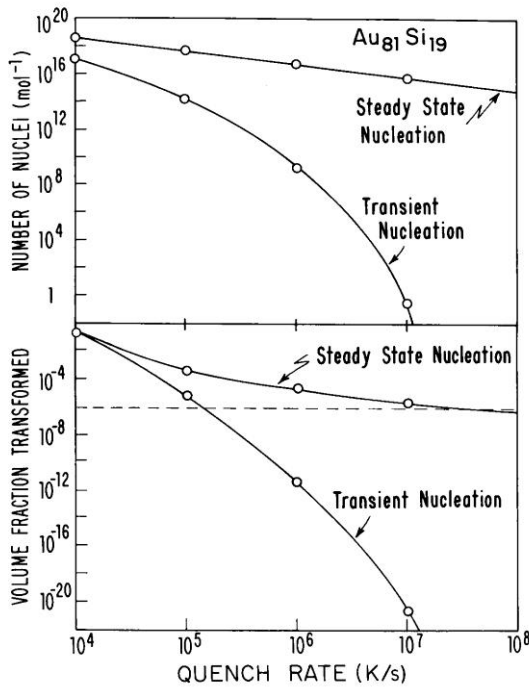


Transient effects on glass formation



Transient effects on glass formation

— rapid quenching ( $10^5$  -  $10^6$  K  $\text{s}^{-1}$ ) needed for glass formation in some metallic systems





## Mechanism of Nucleation Catalysis

This has been most thoroughly studied for **Al-5Ti-1B** —

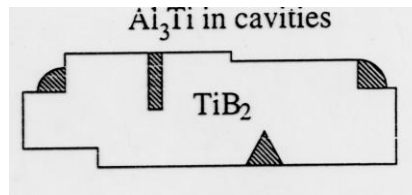
- $\text{TiB}_2$  particles survive in alloys with low solute contents – but appear not to be good nucleants
- $\text{Al}_3\text{Ti}$  particles are very good nucleants (peritectic reaction) – but do not survive in liquid aluminium

Therefore it has been suggested that some sort of **combined action** is necessary

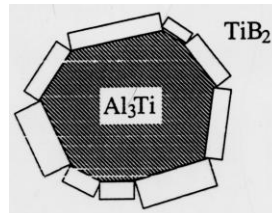
-- stabilization of  $\text{Al}_3\text{Ti}$  by  $\text{TiB}_2$

**3 suggestions for how this might happen —**

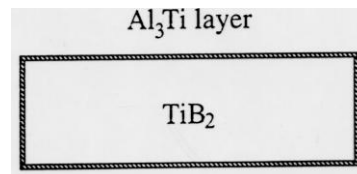
1. Cavity Theory



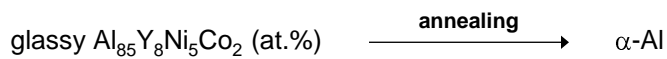
2. 'Hulk' Theory



3. Adsorption Theory



## Study of Heterogeneous Nucleation using a Metallic Glass

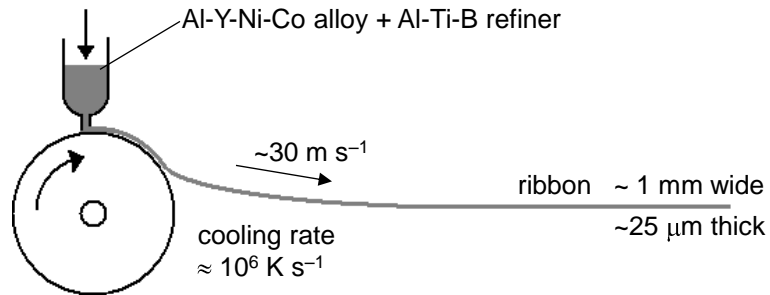


Devitrification is analogous to solidification

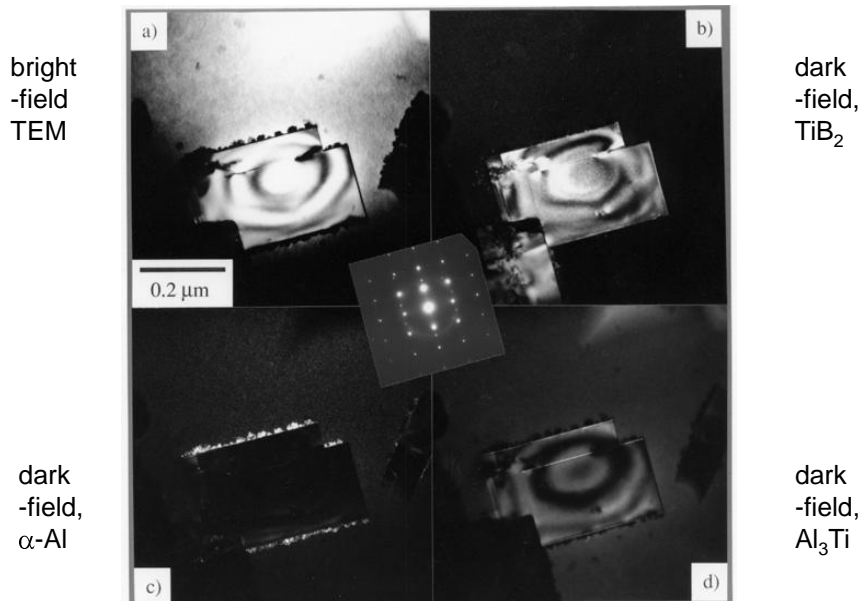
**But:**

- greatly slower ( $\sim 10^{-16}$  x)
- can be interrupted
- no convection
- uniform temperature
- suitable for microstructural study

## Melt-Spinning of Metallic Glass



- ⇒ glassy  $\text{Al}_{85}\text{Y}_8\text{Ni}_5\text{Co}_2$  (at.%), with trace Ti, and embedded particles of  $\text{TiB}_2$
- ⇒ nucleation and growth of  $\alpha$ -Al on the particles during the early stages of the quench, but growth is quickly stifled



[Schumacher, Greer et al., *Mater. Sci. Technol.* **14** (1998) 394.]

## Results of the TEM Study

- $\text{TiB}_2$  has a coating of  $\text{Al}_3\text{Ti}$
- simple orientation relationships --  
close-packed planes (and directions) are parallel in the 3 phases

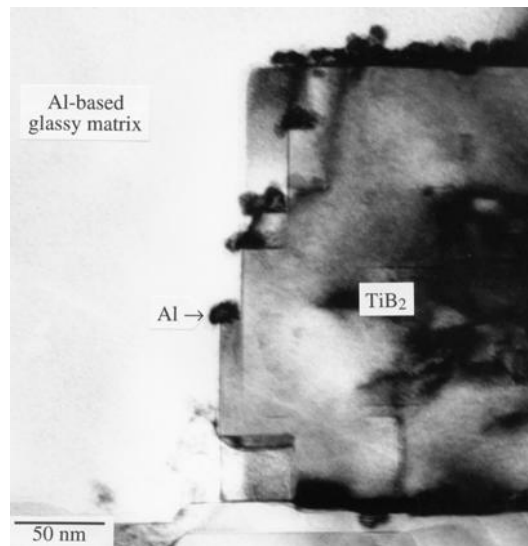
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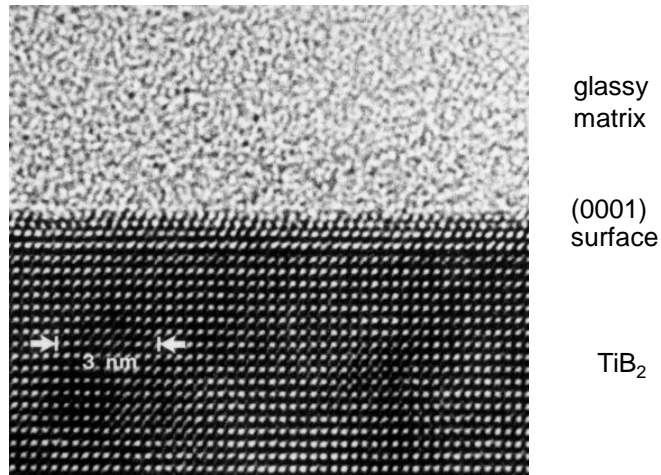
<b><math>\text{TiB}_2</math></b>		<b><math>\text{Al}_3\text{Ti}</math></b>		<b><math>\alpha\text{-Al}</math></b>
(0001)		(112)		(111)

---

- nucleation is only on (0001) – no preference for ledges or cavities

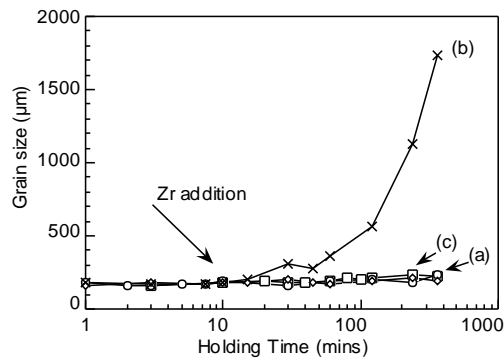
$\alpha\text{-Al}$  crystallites have nucleated and grown on (0001) ledges on the prismatic face of the hexagonal platelet of  $\text{TiB}_2$ . Contact with the prismatic face itself is avoided.





On the surface of the  $\text{TiB}_2$  particle is a thin coherent coating with lattice spacings consistent with  $\text{Al}_3\text{Ti}$ .

[Schumacher & Greer, *Light Metals* 1996, p. 745]

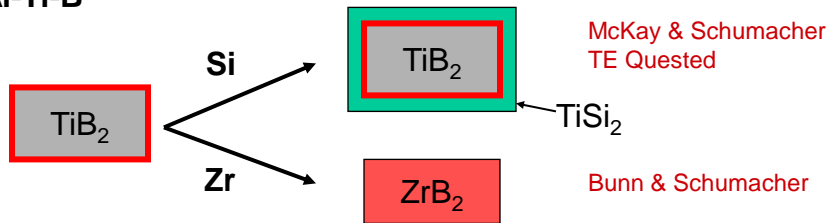


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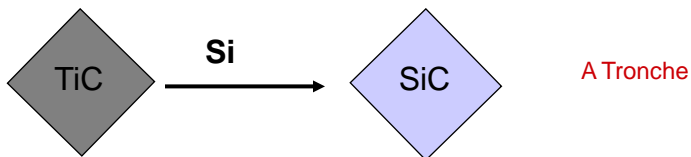
[A.M. Bunn, Ph.D. Thesis (1998), University of Cambridge]

## Poisoning Mechanisms

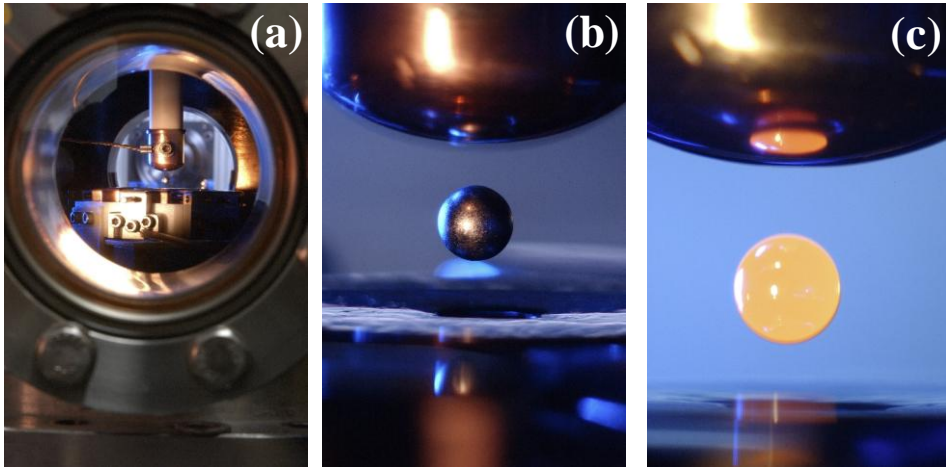
### Al-Ti-B



### Al-Ti-C



- the microscopical studies assist in understanding the mechanisms of potent nucleation catalysis and poisoning
- but they do **not assist** in understanding refiner inefficiency
- or in prediction of **grain size**



- (a) Vacuum chamber and levitation electrodes of the ESL facility at NASA Marshall Space Flight Center
- (b) a solid Zr sphere suspended between the top and bottom electrostatic electrodes
- (c) liquid Zr after laser melting

### Nucleation of solidification —

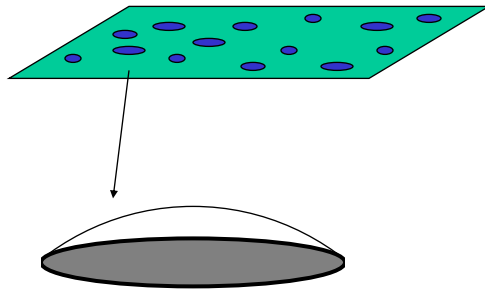
at large supercooling ( $> 100$  K)      at small supercooling ( $< 1$  K)

- |                                 |                                |
|---------------------------------|--------------------------------|
| • focus for fundamental studies | • actual conditions in casting |
| • towards homogeneous           | • potent heterogeneities       |
| • small critical radius         | • large critical radius        |
| • breakdown of classical theory | • classical capillarity        |
| • uncertain model               | • unknown input parameters     |

**Either way** — quantitative modelling difficult

## Classical analysis of heterogeneous nucleation

— formation of spherical-cap nuclei on a planar substrate



Steady state nucleation rate (per unit area) given by:

$$I^s (\text{s}^{-1} \text{m}^{-2}) = N_{\text{surf}} kZ \exp\left(\frac{-W_{\text{het}}^*}{k_B T}\right)$$

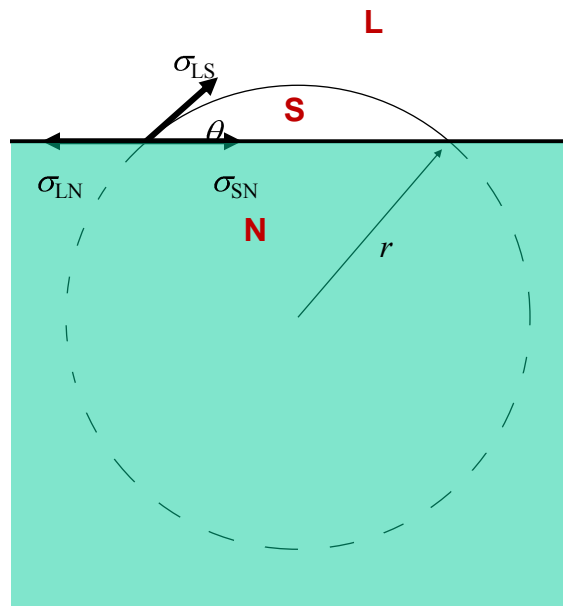
analysing the spherical cap —

$$W_{\text{het}}^* = W_{\text{hom}}^* f(\theta)$$

$$W_{\text{hom}}^* = \frac{16\pi\sigma_{\text{LS}}^3}{3\Delta G_{\text{V}}^2}$$

$$f(\theta) = \frac{2 - 3\cos\theta + \cos^3\theta}{4}$$

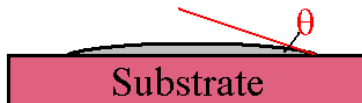
$$r_{\text{het}}^* \equiv r_{\text{hom}}^* \equiv r^* = \frac{-2\sigma_{\text{LS}}}{\Delta G_{\text{V}}}$$



## Prediction of Heterogeneous Nucleation Kinetics

Quantitative prediction is not normally considered to be possible.

- The input parameters for the classical theory are not well known (interfacial energies and contact angle  $\theta$ ).



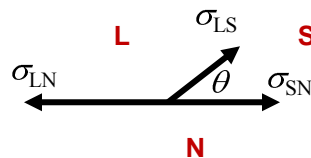
- The spherical-cap model itself breaks down for **potent nucleation** catalysis (low  $\theta$ ) -- of interest for inoculation. [Cantor, *Mater. Sci. Eng. A*, **178** (1994) 225]
- Predictive modelling may be further hindered by the **variety** of potency of the nucleant particles.

### Contact angle

$$\sigma_{LS} \cos \theta = \sigma_{LN} - \sigma_{SN}$$

But a contact angle is defined only if —

$$\sigma_{LS} \geq |\sigma_{LN} - \sigma_{SN}|$$

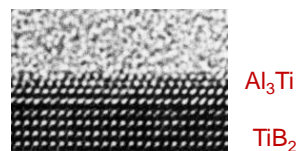
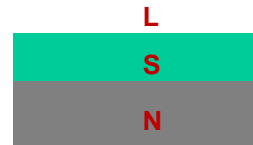


Otherwise, either the liquid or the solid “wets” the nucleant substrate

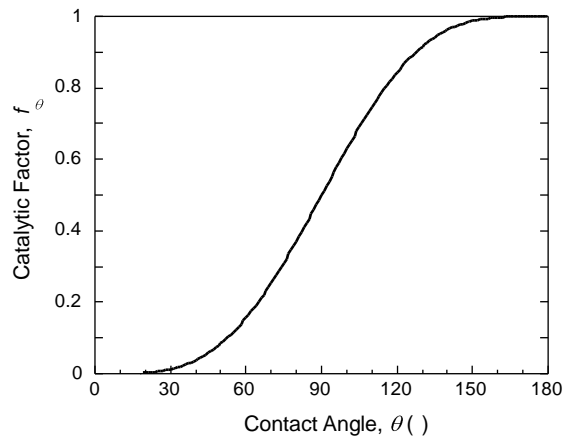
for example if  $\sigma_{LN} > \sigma_{LS} + \sigma_{SN}$

The solid coating (wetting layer) is stable even for  $T > T_m$

Even without a wetting layer, there may be **adsorption** on the substrate



Nucleation barrier disappears as contact angle tends to zero

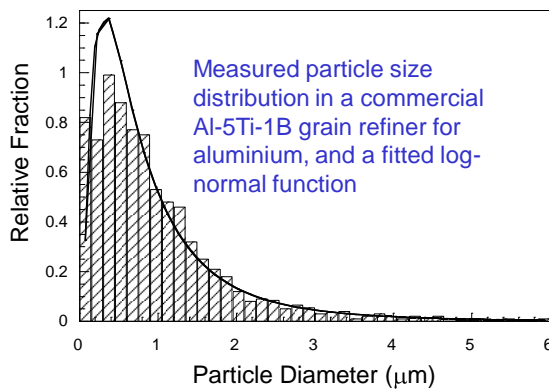


- with **wetting** or **adsorption** there is also **no nucleation barrier** for the formation of solid on the substrate

At **small supercooling** the critical radius is **large**

e.g. for Al, with  $\Delta T = 0.2$  K,  $r^* = 1.4$   $\mu\text{m}$

— similar to typical inoculant particle diameters

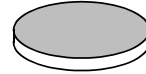


Therefore **substrate-size effects** are important



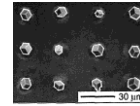
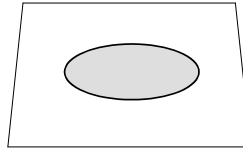
## Finite-size substrates

- could be the active **face** of a nucleant particle (e.g. {0001} of  $\text{TiB}_2$  particles in Al) —



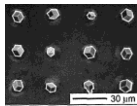
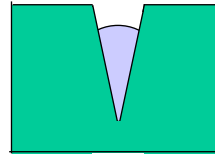
hexagonal particle approximated as a circular disc

- could be an active **patch** on a substrate —



Aizenberg et al.  
*Nature* **398** (1999) 495

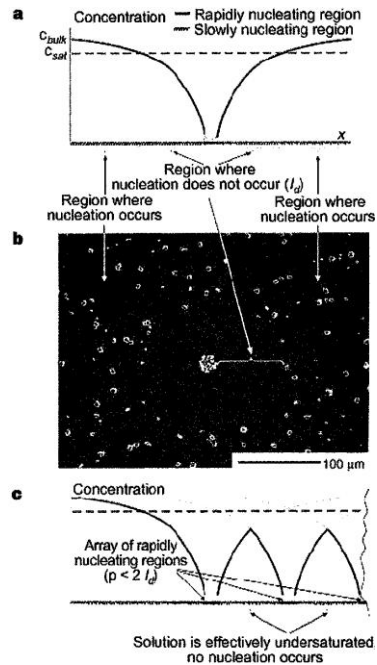
- could represent the case of growth from a **cavity** —



Aizenberg et al.  
*Nature* **398** (1999) 495

Crystallization of calcite from solution:

— depletion of solute concentration is important



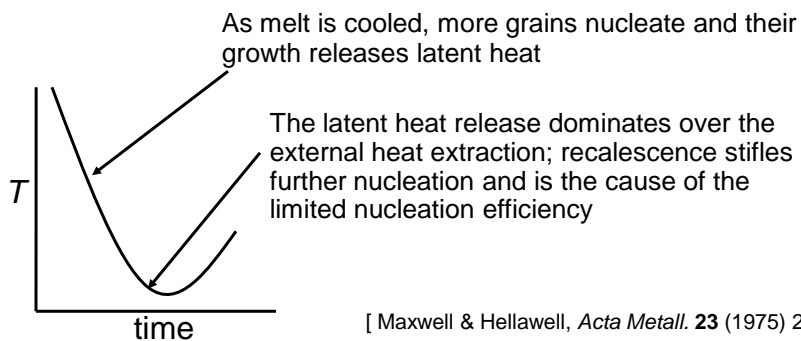
## Length Scales in a Typical Casting

- distance between particles  $\approx 10 \mu\text{m}$
- solute diffusion length  $\approx 1 \mu\text{m}$
- thermal diffusion length  $\approx 1 \text{cm}$

## Maxwell-Hellawell Model

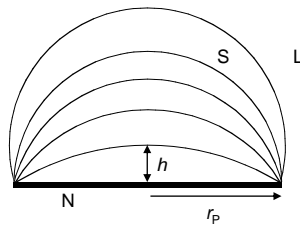
Noted that:

- typical thermal diffusion length  $\gg$  grain diameter
- therefore can assume a spatially isothermal melt



[ Maxwell & Hellawell, *Acta Metall.* **23** (1975) 229.]

- with **wetting** or **adsorption** there may be **no nucleation barrier** for the formation of solid on the substrate
- but the solid is not yet a **transformation nucleus**, because there is a barrier to **free growth**
- as the solid thickens ( $h$  increases), the radius of curvature of the LS interface  $r_{LS}$  **first decreases** — possible only if  $\Delta T$  **increases**



The critical condition (maximum  $\Delta T$ ) is when the solid forms a **hemisphere** ( $r_{LS} = h$ )

## Athermal nucleation

- first defined by Fisher, Hollomon & Turnbull (1950)
- **embryos** are “automatically promoted to nuclei” when the critical size decreases, and sweeps past their own size
- not important for homogeneous nucleation, but is **important for heterogeneous nucleation on potent substrates**

Athermal nucleation, i.e. the onset of free growth, occurs when

$$\Delta T_{fg} = \frac{-2\sigma_{LS}}{\Delta S_v r_p}$$

(for a circular substrate of radius  $r_p$ )  
(using  $\Delta G_v = \Delta S_v \Delta T$ )

— i.e. grain initiation occurs **first** on the **largest** nucleant substrates

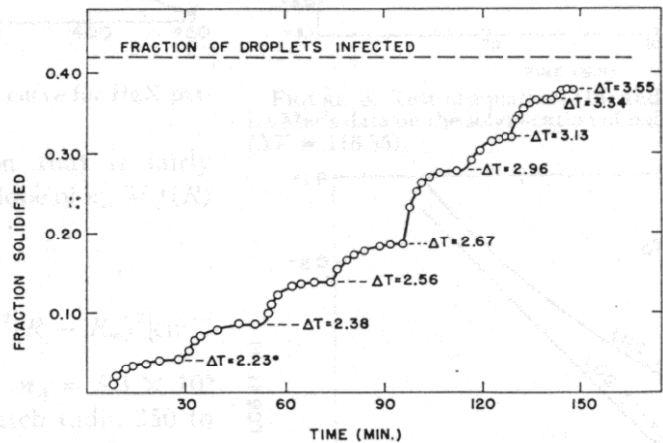


FIGURE 1. Fraction of mercury droplets solidified with successively increasing supercooling. 42 per cent of the droplets are infected with HgX patches. (Sample B).

Turnbull [*Acta Metall.*, 1 (1953) 8] found that in some of his mercury emulsions, the fraction of mercury droplets solidifying was dependent on **supercooling**, not **time**.

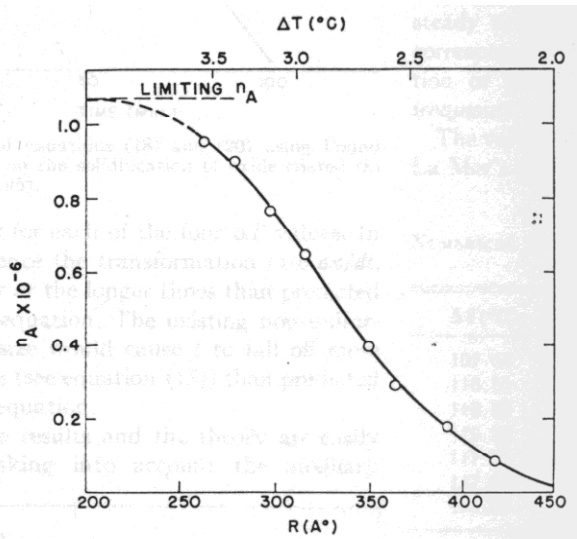
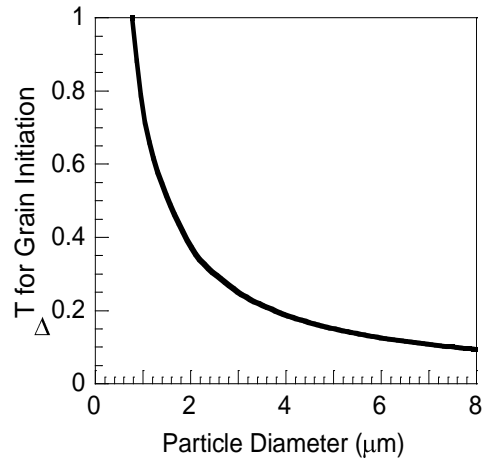


FIGURE 2. Calculated size distribution curve for HgX patches on mercury droplets of sample B.

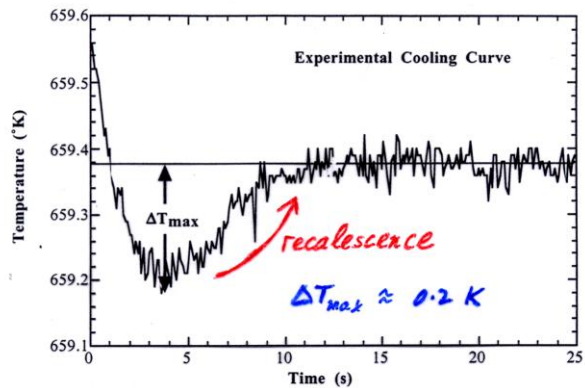
From the athermal nucleation data, Turnbull derived the size distribution of **nucleant patches** on the droplet surfaces.

## Free-Growth Model

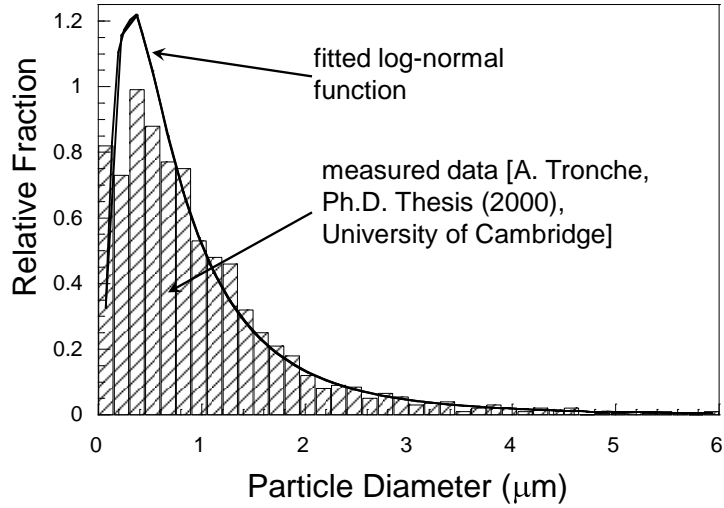
- For the particle sizes known to be present, the free-growth undercooling is comparable with measured undercooling:



In standard grain-refining tests, a very small undercooling of  $\sim 0.2$  K is found --

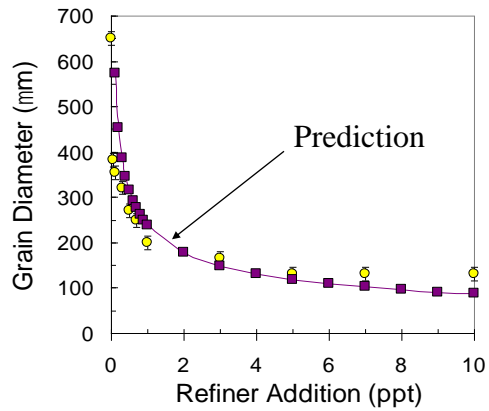


The size distribution of  $TiB_2$  particles in a commercial Al-5Ti-1B refiner approximates to a log-normal function:



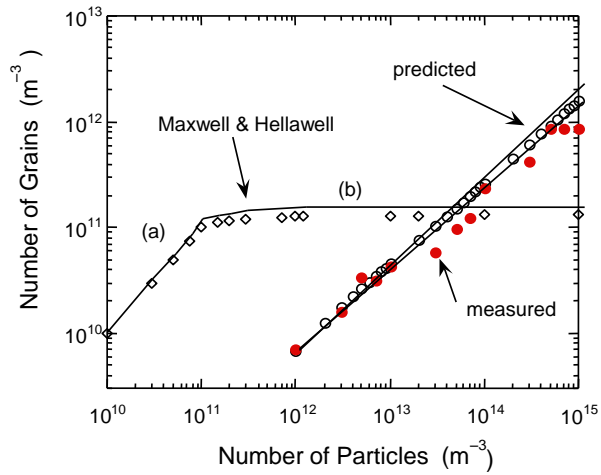
## Test of the Free-Growth Model

Good fit to results of TP-1 tests  
(cooling rate  $\approx 3.5 \text{ K s}^{-1}$ )  
with different addition  
levels of refiner



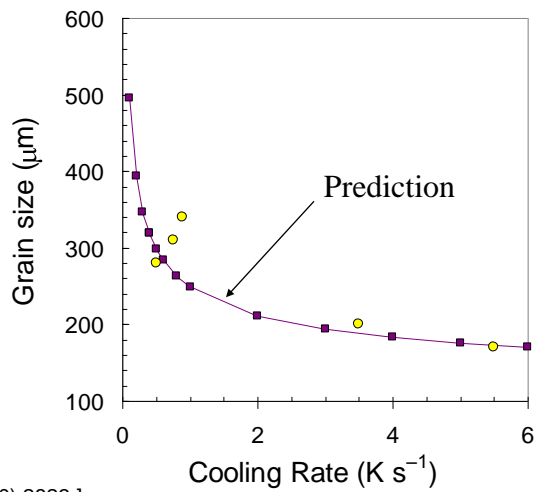
[Greer et al., *Acta Mater.* **48** (2000) 2823.]

Directly predicts that refiner efficiency (percentage of particles nucleating grains) is very low



[Greer et al., *Acta Mater.* **48** (2000) 2823.]

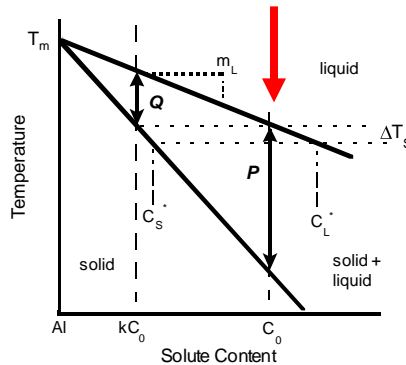
Reasonable fit to results of TP-1 tests modified to vary cooling rate



[Greer et al., *Acta Mater.* **48** (2000) 2823.]

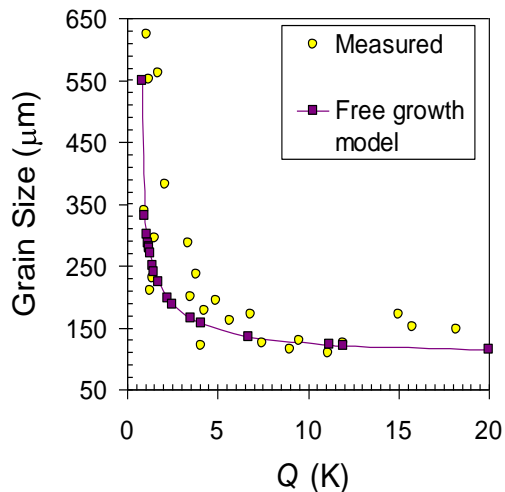
## Importance of Solute Content

- the **solute content** is important for grain refinement by inoculation
  - the continuing nucleation of grains in the melt requires **undercooling**
  - undercooling is possible only because **solute partitioning** restricts the growth of grains already nucleated
- 
- in early work the freezing range **P** was thought to be important
  - but the key parameter is **Q**, defined by:
 
$$Q = m(k - 1)C_0$$
  - for straight liquidus and solidus, values of **Q** are additive for all solutes



Measurements of Spittle & Sadli [*Mater. Sci. Technol.* **11** (1995) 533] show importance of solute content represented by the **growth restriction factor**:

$$Q = m(k - 1)C_0$$



[Greer et al., *Acta Mater.* **48** (2000) 2823.]

## Aspects of Growth Restriction

The **growth-restriction factor** is related to the fraction solidified:

$$\left(\frac{df_s}{dT}\right)_{f_s \rightarrow 0} = -\frac{1}{Q}$$

and it governs the crystal growth velocity  $V$ , such that:

$$V \propto \frac{D_s}{Q}$$

— at a given undercooling and grain diameter

- in inoculation, the solute content of the **added refiner** is significant
- good refiners contain solutes with particularly high values of  $Q/C_0 = m(k-1)$
- for example, the excess **Ti content** of Al-Ti-B refiners is very important for their performance

## Growth-Restricting Effects of Common Solutes

**in Al —**

solute	$m$	$k$	$m(k-1)$
Cr	2.6	1.75	1.9
Cu	-2.5	0.145	2.1
Fe	-2.925	0.03	2.4
Mg	-5.84	0.48	3.0
Mn	-1.2	0.62	4.6
Ni	-3.5	0.004	3.5
Si	-6.62	0.12	5.8
<b>Ti</b>	<b>25.63</b>	<b>7</b>	<b>154</b>
Zn	-1.65	0.43	0.9

**in Mg —**

( $m$  in K/wt.%)

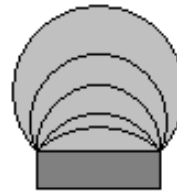
solute	$m$	$k$	$m(k-1)$
Al	-6.87	0.37	4.3
Ca	-12.67	0.06	11.9
Ce	-2.86	0.04	2.7
Cu	-5.37	0.02	5.3
Si	-9.25	~0.00	9.2
Sr	-3.53	0.006	3.5
Y	-3.40	0.50	1.7
Zn	-6.04	0.12	5.3
<b>Zr</b>	<b>6.90</b>	<b>6.55</b>	<b>38.3</b>

Most solutes have **negative  $m$  — eutectic systems**

A few solutes (including the most effective growth restrictors, Ti in Al and Zr in Mg) have **positive  $m$  — peritectic systems**

## Free-Growth Model

- the critical (maximum undercooling) condition for free growth of a grain is when the interface with the liquid is **hemispherical**
- this is analogous to the critical (maximum pressure) condition for blowing a **bubble** out of a tube
- in this way the free-growth model applies also to bubble formation in **beer** and **champagne**
- as the drink goes 'flat', the diameter of nucleant sites above which bubbles can form increases steadily



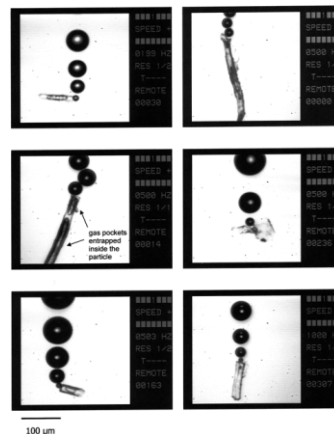
## Bubbles in Champagne

In champagne the supersaturation ratio of  $\text{CO}_2$  is ~5

This is insufficient for homogeneous nucleation, or even for heterogeneous nucleation at reasonable contact angle

At usual supersaturation, the radius of the critical nucleus is  $0.2 \mu\text{m}$

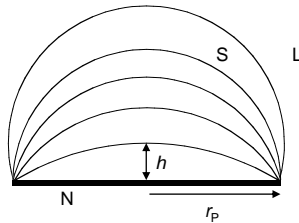
[Liger-Belair, *Sci. Amer.* Dec. 2002; *Langmuir* **18** (2002) 1294.]



Bubbles in champagne rising from gas-filled cavities in cellulose fibres

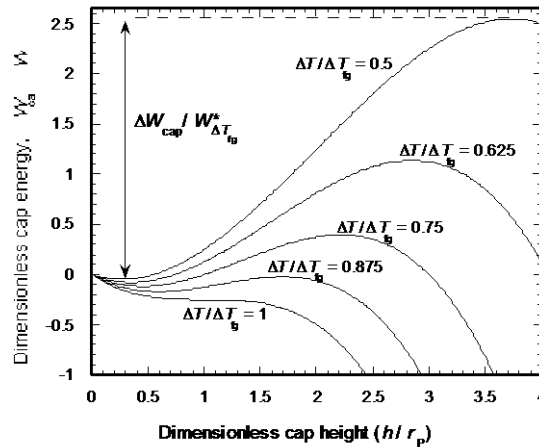
## Competition between athermal and thermal nucleation

- does thermal activation of free growth happen before the  $\Delta T$  for barrierless growth  $\Delta T_{fg}$  is reached?
- we calculate the work of formation of the solid cap as a function of cap height  $h$  —



The critical condition (maximum  $\Delta T$ ) is when the solid forms a **hemisphere** ( $r_{LS} = h = r_p$ )

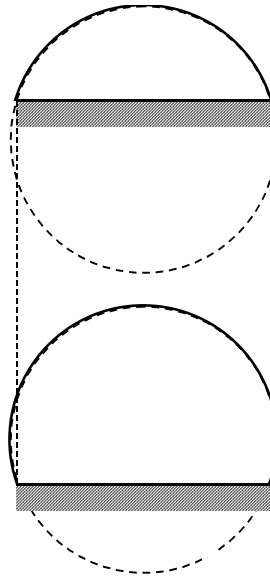
T. E. Quested & A. L. Greer, *Acta Mater.* **53** (2005) 2683.



$$\frac{W_{\text{cap}}}{W^*_{\Delta T_{fg}}} = -\frac{1}{4} \left( \frac{\Delta T}{\Delta T_{fg}} \right) \left( \frac{h}{r_p} \right)^3 + \frac{3}{4} \left( \frac{h}{r_p} \right)^2 - \frac{3}{4} \frac{\Delta T}{\Delta T_{fg}} \frac{h}{r_p}$$

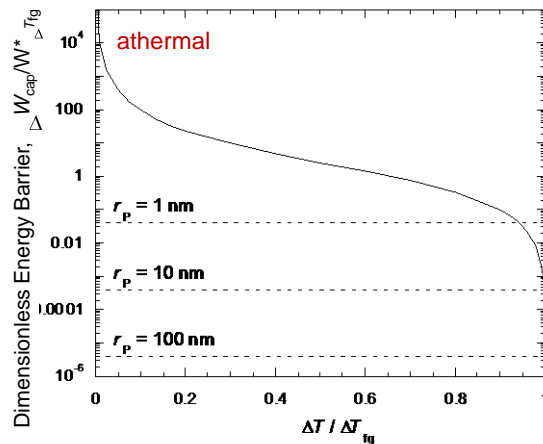
Dimensionless work of formation of the solid cap on a circular nucleant area as a function of cap height for selected values of dimensionless undercooling ( $\Delta T / \Delta T_{fg}$ ).

Metastable configuration of the solid cap when the work of formation is **minimum**



Unstable configuration of the solid cap when the work of formation is **maximum**

In each case the LS interface is in **equilibrium**, as  $r_{LS} = r^*$



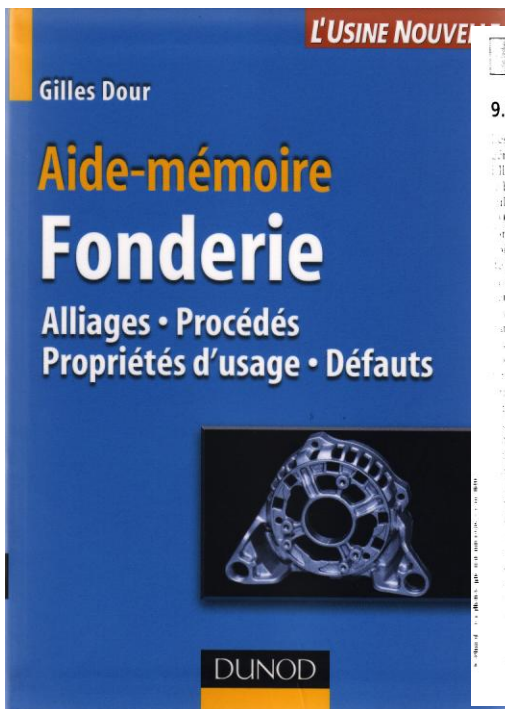
T. E. Quested & A. L. Greer, *Acta Mater.* **53** (2005) 2683.

The critical work of nucleation as a function of undercooling for a solid cap forming on a circular nucleant area. The dashed lines indicate values of the critical work below which thermal activation of nucleation precedes the onset of free growth.

For a  $1.5 \mu\text{m}$  diameter inoculant particle in Al, thermal activation becomes significant only within 1 part in  $10^8$  of  $\Delta T_{fg}$

We can conclude that for inoculation of Al alloys, for example:

- grain initiation is **deterministic**, governed by  $\Delta T$ , but independent of time
- the free-growth model is valid, as are similar nucleation laws used on solidification modelling



## 9.2 Théorie de la croissance libre

Les pratiques d'inoculation varient beaucoup d'un alliage à l'autre. En règle générale la pratique consiste à introduire des particules solides dans le bain. Elles peuvent être introduites sous forme de poudre qui reste solide dans le bain suffisamment longtemps pour être actives (ferrosilicium pour l'inoculation de la fonte GS, TiC stable pour un pourcentage de Ti supérieur à 0,1 % dans le bain) ou sous forme solide qui se dissout puis réagit pour former des particules en tout début de refroidissement. Une troisième pratique consiste à dissoudre un *master alloy*, alliage riche en élément primaire de l'alliage coulé et qui contient des particules formées et piégées lors de la solidification (par exemple, Al-Ti-B ou Al-Ti-C). Les premières sont généralement introduites au dernier moment, comme par exemple, dans le canal de coulée pour les fontes. Les secondes et les troisièmes le sont dans le bain, quelques minutes (pour laisser le temps à la dissolution) avant le coulé. Pour l'instant les mécanismes exacts de dissolution ou de réaction des particules ne sont pas toujours bien connus. On parle plutôt de temps d'application optimal sans toujours savoir ce qui se cache derrière. En règle générale, les inoculants n'ont qu'une efficacité très faible puisque moins de 1 % des particules introduites donnent naissance à un grain. Ceci est attribué généralement à la recalescence : la chaleur latente dégagée lors de la formation et la croissance d'un grain anéantit la germination de tout autre grain dans un rayon de l'ordre de 100 à 1 000 fois la taille de la particule à cause de l'abaissement de la surfusion.

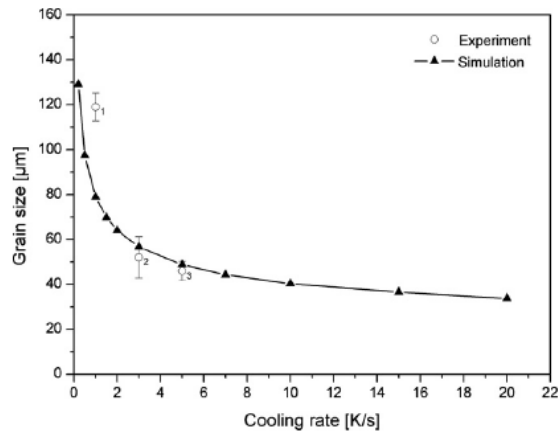
Des discussions encore très animées existent sur l'effet de la taille des particules. Des investigations récentes sur la germination dans des verres métalliques réchauffés sous microscope électronique à transmission (TEM) montrent que les germes hétérogènes se forment sur certains plans cristallographiques des substrats et que ces germes peuvent être plus petits que la taille de la particule (figure 9.2).

Les germes stables qui existent ne donnent cependant pas forcément naissance à un grain. Pour cela il faut que chaque germe grossisse latéralement pour épouser toute la surface de mouillage de la particule. Ensuite la croissance doit continuer au-delà du contact avec le substrat, en mode de croissance libre. Or, comme il est détaillé dans la figure 9.3, la croissance ne s'effectue pas dans l'extension complète sur la surface du germe (position 3 sur la

SCIENCE DE L'INGÉNIEUR UTILES EN Fonderie

## Application of the free growth model to Mg alloys —

grain refinement of AZ31 with SiC particles



[R. Günther, Ch. Hartig & R. Bormann, *Acta Mater.* **54** (2006) 5591.]



### Northern Wood Frog

*Rana sylvatica*

— the only frog found north of the Arctic circle

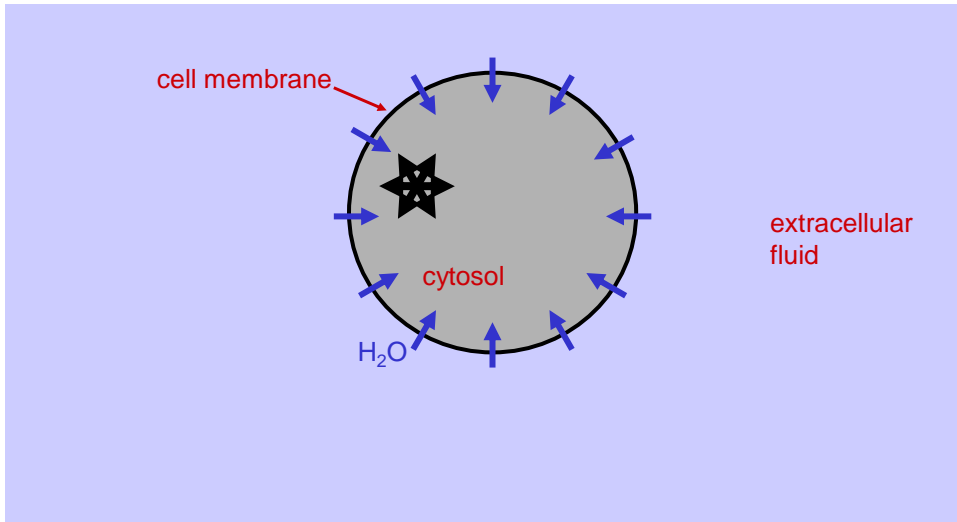
— in winter is completely solid, 45% ice

— when frozen, the frog's breathing, blood flow and heartbeat stop

## Ice formation inside a cell

— is fatal

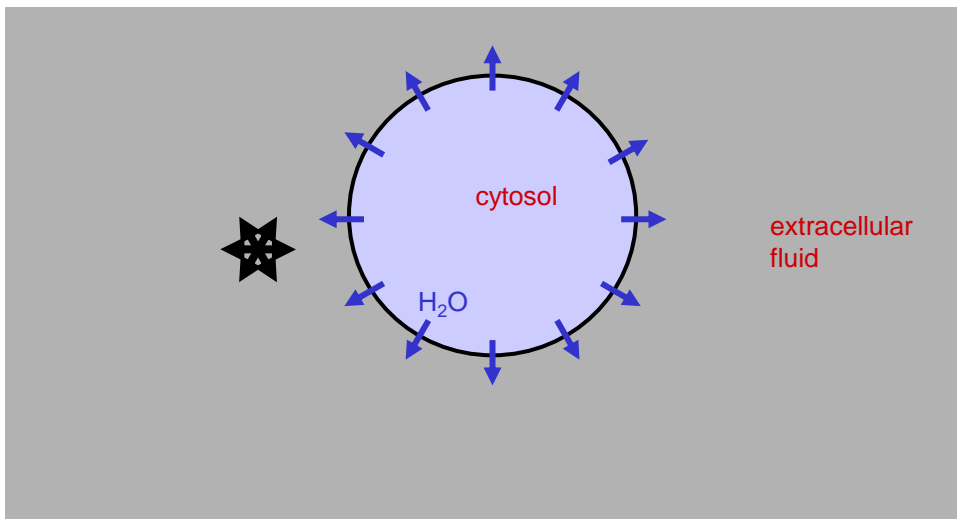
- the salt concentration rises in the remaining cytosol
- water is drawn into the cell by osmosis from the extracellular fluid
- the cell continues to swell and eventually bursts



## Ice formation in the extracellular fluid

— is beneficial

- the salt concentration rises in the extracellular fluid
- water is drawn from the cell by osmosis from the extracellular fluid
- the cell shrinks and the cytosol is dehydrated into a sugar glass



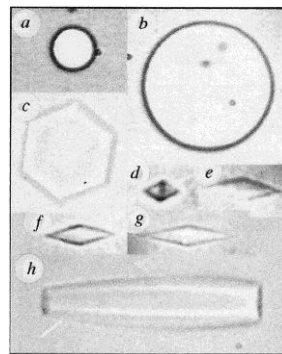
## Ice-nucleating agents (INAs)

- are found in many ectothermic living systems
- **bacteria** use them to promote **frost damage** on leaves
  - releases nutrients
- **insects** and **amphibians** use them to become **freeze-resistant**, by promoting ice formation **outside their cells**
  - prevents freezing inside the cells (fatal if it occurs)
  - freeze concentration of extracellular fluid
  - draws water from cells by osmosis
  - cells congeal to a glassy state
- typical biogenic INAs nucleate ice at  $\Delta T = 3$  to  $12$  K
  - **why so bad?**

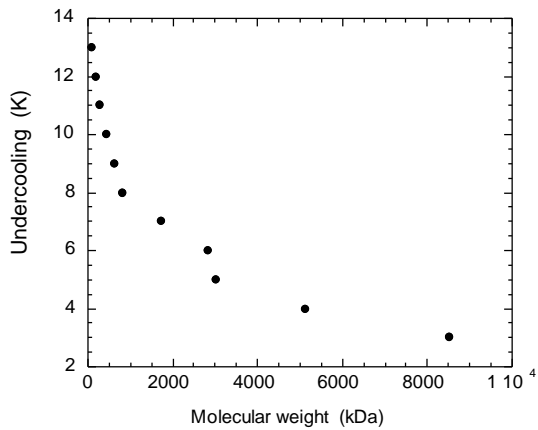
## Ice crystals

Their growth form is modified by, for example, the presence of anti-freeze proteins (AFPs) in the solution.

In the absence of AFPs, small ice crystals are circular discs with the c-axis normal to the substrate.



[Jia et al., *Nature* **384** (1996) 285]

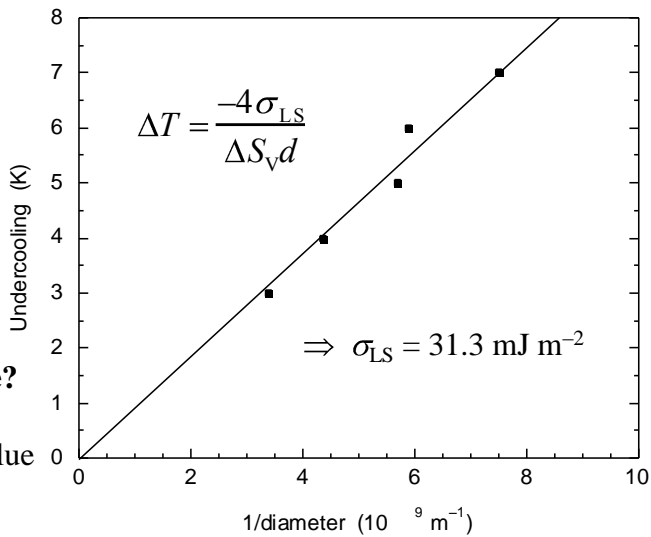


Critical undercooling for ice nucleation vs the molecular weight of the ice-nucleating agent for a particular bacterial strain *P. syringae*.

[Govidarajan & Lindow, *Proc. Natl. Acad. Sci. USA* **85** 1334 (1988)]

Burke & Lindow: *Cryobiology* **27** (1990) 80

— data on supercooling and diameter of INA discs



**$\sigma_{LS}$  for water/ice?**  
 20 - 44 mJ m<sup>-2</sup>  
 recommended value  
 30 mJ m<sup>-2</sup>

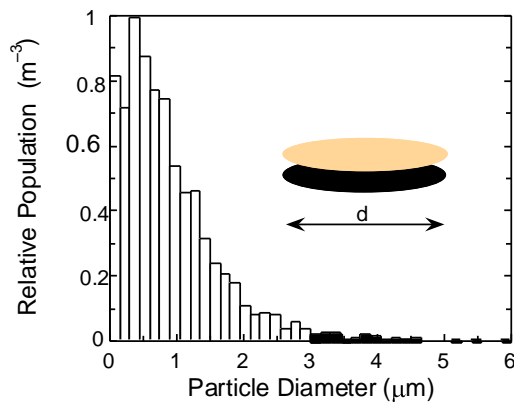
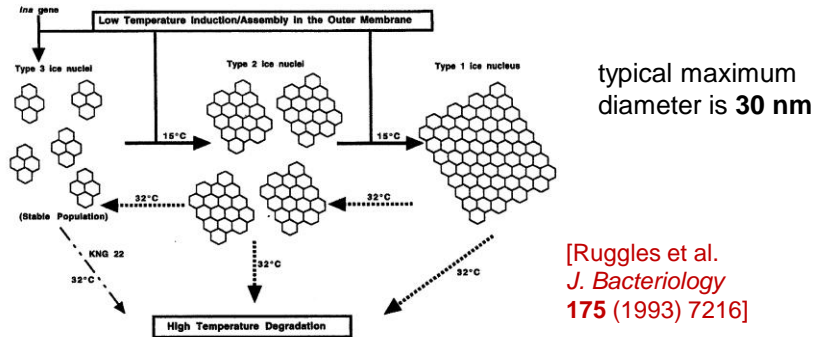
Franks (1982)

## INAs are rather unusual proteins —

- they maximize their flatness

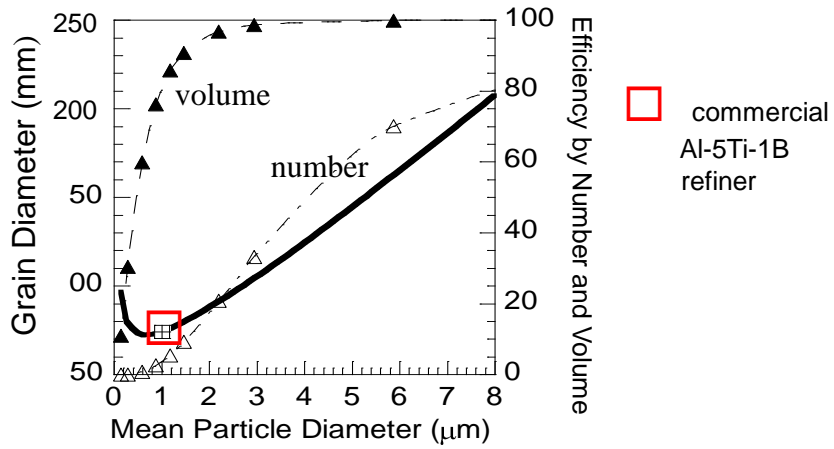
[Yang et al. *Biophysical J.* **74** (1998) 2142]

- they aggregate to increase their effective size, a factor contributing to cold conditioning —



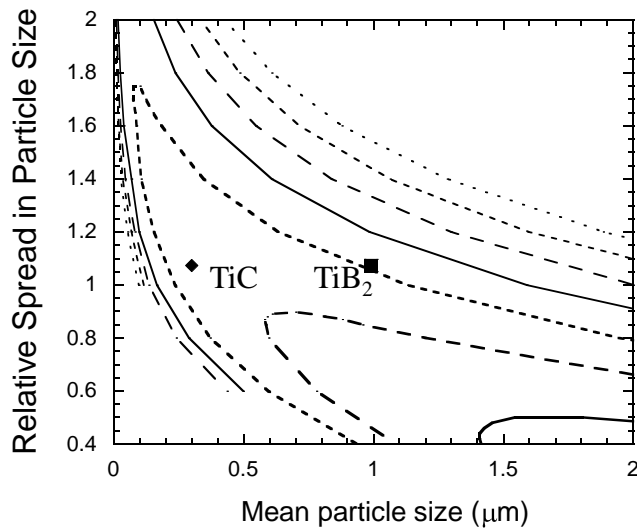
## How optimal is a commercial refiner?

- are there possibilities for design of improved refiners?



[Quested, Greer & Cooper, *Mater. Sci. Forum* **396-402** (2002) 53]

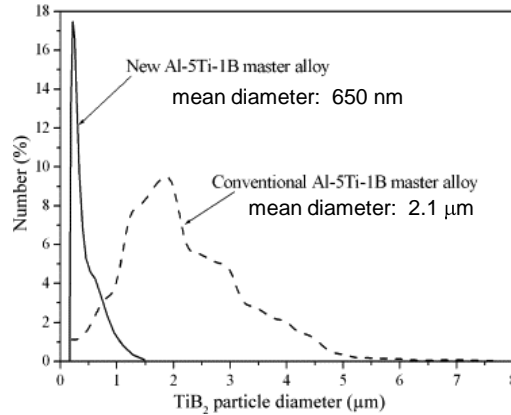
### Contour Map of Grain Size



[Quested & Greer, *Acta Mater.* **52** (2004) 3859]

## Improvement of conventional Al-5Ti-1B refiner

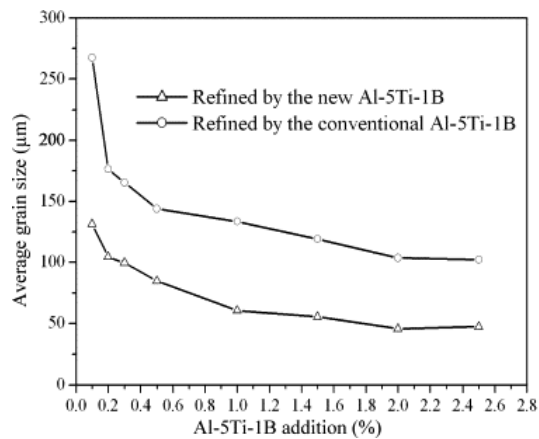
— application of high-intensity ultrasound during the reaction of  $K_2TiF_6$  and  $KBF_4$  salts, shortens the reaction time (60 min  $\rightarrow$  4 min) and gives  $TiB_2$  particles with smaller mean diameter and narrower size distribution:



Y. Han, D. Shu, J. Wang & B. Sun: *Mater. Sci. Eng. A* **430** (2006) 326.

— giving improved refinement:

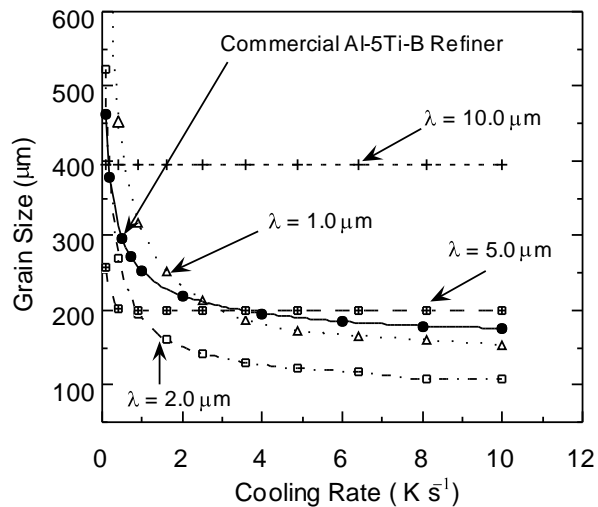
- grain size as small as **45  $\mu m$**
- compared to **100  $\mu m$**  minimum for conventional refiner



Y. Han, D. Shu, J. Wang & B. Sun: *Mater. Sci. Eng. A* **430** (2006) 326.

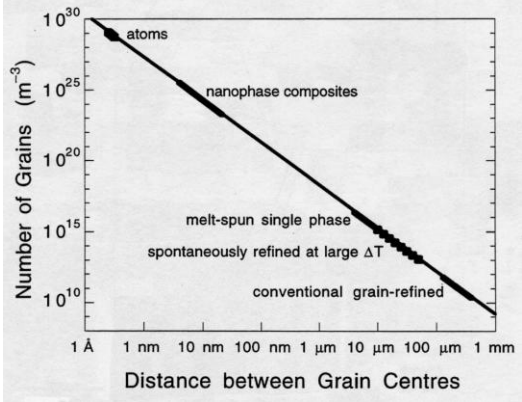
- for a given width of size distribution, there is a defined mean particle diameter giving **minimum grain size**
- empirical development has led to commercial refiners having mean particle diameters **near this optimum**
- **number efficiency** of the refiner is **low**
- but its **volume efficiency** is **high**

The larger the mean diameter of the  $TiB_2$  particles, the greater the insensitivity of the grain size to cooling rate — important for uniformity of grain structure.

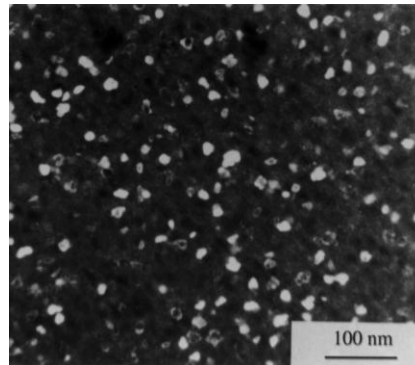
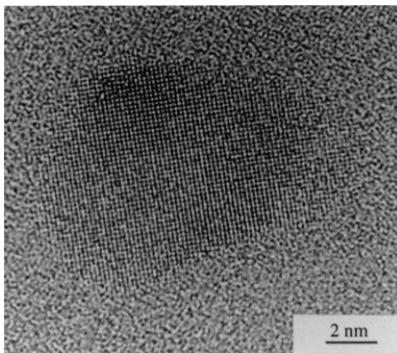


[Tronche & Greer, *Light Metals 2000*, p. 827]

## Nanometre-Scale Grain Structures

- at high addition levels grain refinement saturates
  - inoculation of Al gives a smallest grain size of  $\sim 100 \mu\text{m}$
  - smaller grains can be obtained by rapid solidification
  - the finest grains are obtained when **recalcescence is suppressed**
- 
- this is achieved by crystallizing a metallic glass (**devitrification**)
  - $1 \text{ cm}^3$  of the **nanophase composite** has more grains than the entire annual production of conventional aluminium alloys!

$\text{Al}_{88}\text{Ni}_4\text{Y}_8$  (at.%) rapidly solidified by melt-spinning into a fully glassy state and then heated through the first devitrification to give a dispersion of  $\alpha$ -Al nanocrystals in a glassy matrix.

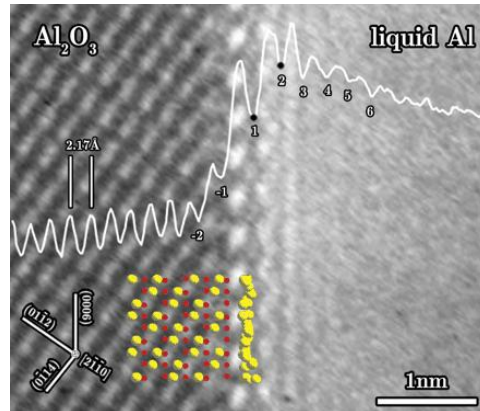


The nanocrystals are so small that they are dislocation-free. Their formation increases the yield stress of the material, without embrittlement.

[Z. C. Zhong, Ph.D. Thesis (1997), University of Cambridge]

## Layering in liquid aluminium adjacent to solid alumina

Layered contrast visible in liquid Al at 750°C next to a (0001) surface of alumina. The atom positions in the  $\text{Al}_2\text{O}_3$  (red for oxygen and yellow for aluminium) were determined by contrast matching between simulated and experimental images at different objective lens defocus and specimen thickness values. The first layer of liquid atoms is shown schematically.



[S.H. Oh, Y. Kauffmann, C. Scheu, W.D. Kaplan, M. Rühle, Ordered Liquid aluminum at the interface with sapphire *Science* **310** (2005) 661 - 663]

Yet, despite such order in the liquid, aluminium can be supercooled by 175 K in contact with alumina.

[A.L. Greer: *Nature Materials* **5** (2006) 13-14]  
— citing B.A. Mueller & J.H. Perepezko: *Metall. Trans. A* **18A** (1987) 1143.

## Conclusions

Microscopical studies can reveal mechanisms of **nucleation** and **poisoning**

### For Al-Ti-B refiners

- Nucleation catalysts are thin hexagonal platelets of  $\text{TiB}_2$
- Both **crystallography** and **chemistry** are important
- Nucleation occurs only on basal {0001} faces of  $\text{TiB}_2$  particles, with a clear orientation relationship: in  $\text{TiB}_2$ ,  $\text{Al}_3\text{Ti}$ , and  $\alpha\text{-Al}$ , the **close-packed planes and directions are parallel**
- Nucleation occurs only when there is **excess Ti** in the melt, giving a **coating of  $\text{Al}_3\text{Ti}$**  on the  $\text{TiB}_2$
- Poor refiners can be improved by holding in the melt to develop a coating

### Poisoning of Al-Ti-B refiners by zirconium

- $\text{TiB}_2$  is converted to  $\text{ZrB}_2$  and there is no coating on the particles
- This poisoning can be avoided by coating the particles with a stable Ta-based aluminide

### Predictions of Grain Size

- In inoculated melts **at most 1%** of the particles nucleate grains
- This inefficiency is caused by release of **latent heat** (Maxwell-Hellawell model)
- For Al alloys, Al-Ti-B refiners are so potent that grain initiation is limited by the **free-growth barrier** rather than by nucleation itself.
- Input to the free-growth model is **measured particle size distributions**
- **Quantitative predictions** can be made for grain size as a function of
  - refiner addition level (Al-Ti-B or Al-Ti-C)
  - cooling rate
  - solute level in the melt

## Optimization of refiners

- Quantitative modelling allows **design of improved refiners**
- There is a defined average particle size to give **minimum grain size**
- Commercial Al-Ti-B refiners:
  - have particle size close to this optimum
  - **are efficient**, measured by volume (rather than number) fraction of added particles

## Conclusions

- TEM can aid in understanding the effectiveness of nucleants under differing conditions; glasses can serve as liquid analogues
- heterogeneous nucleation at very small supercoolings is likely to be dominated by **substrate-size effects**
- this **athermal nucleation** is deterministic, not stochastic, and can be quantitatively modelled if the **particle-size distribution** is known

### For the future, we need —

- a better understanding of heterogeneous nucleation at **moderate supercoolings**
- the link between **templating** the solid and **adsorption**
- **atomistic simulations** are a priority — what is the ordering of a liquid next to a substrate and what is the temperature dependence?