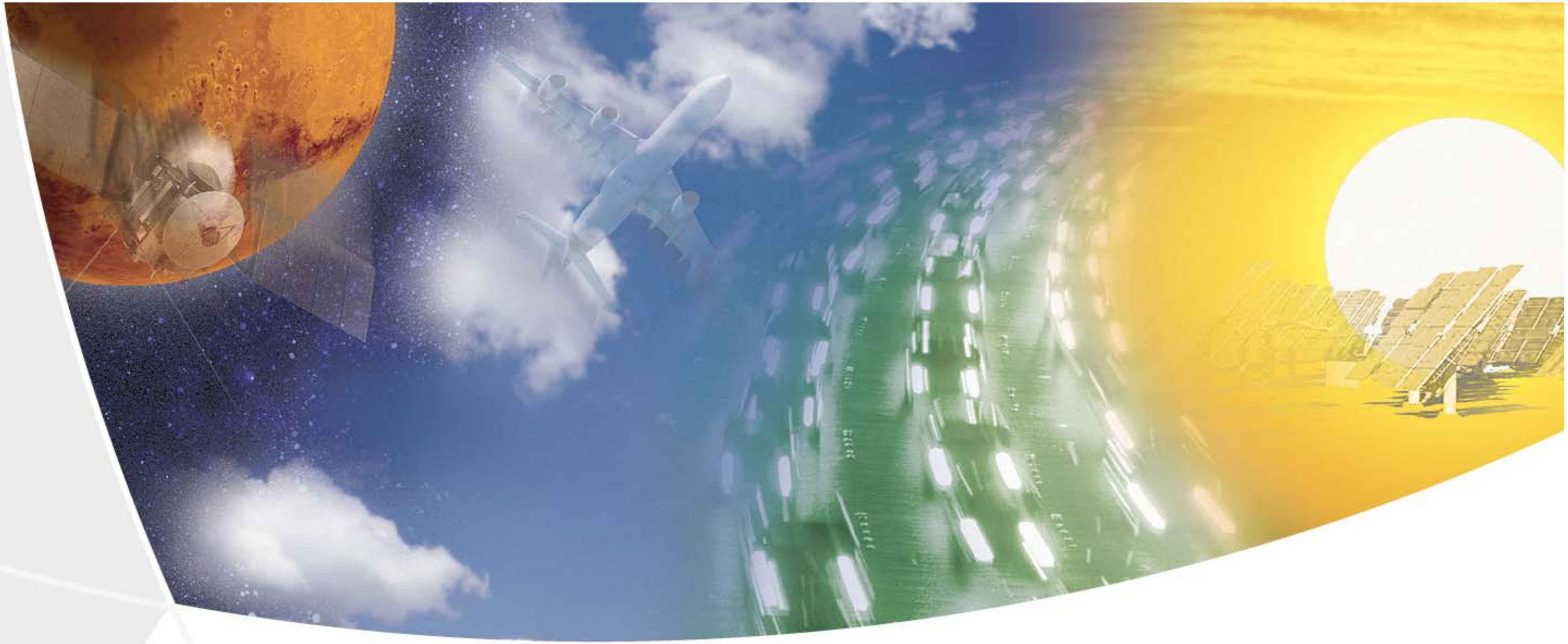

Phase equilibria and phase separation processes in immiscible alloys

Lorenz Ratke, Gudrun Korekt, Sabine Brück, Frank Schmidt-Hohagen,

Galina Kasperovich, Markus Köhler

Institute of Materials Physics in Space, German Aerospace Center, DLR

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in der Helmholtz-Gemeinschaft

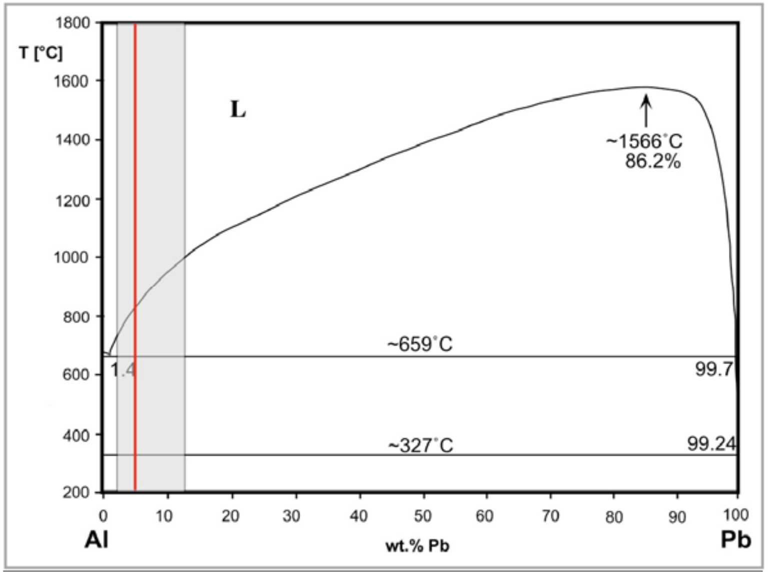
Typical immiscible alloys

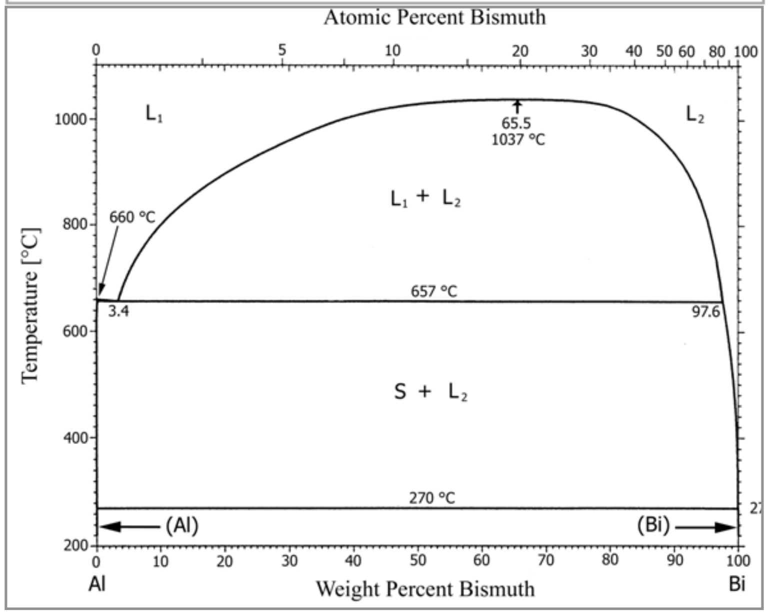
Stable miscibility gaps

- Al-Pb, Al-In, Al-Bi, Al-Cd
- Cu-Pb
- Ga-Bi, Ga-Pb, Ga-Hg
- Zn-Pb, Zn-Bi
- Fe-Ag, Ni-Ag
- and many others

Metastable miscibility gaps

- Cu-Co, Cu-Fe, Cu-Cr



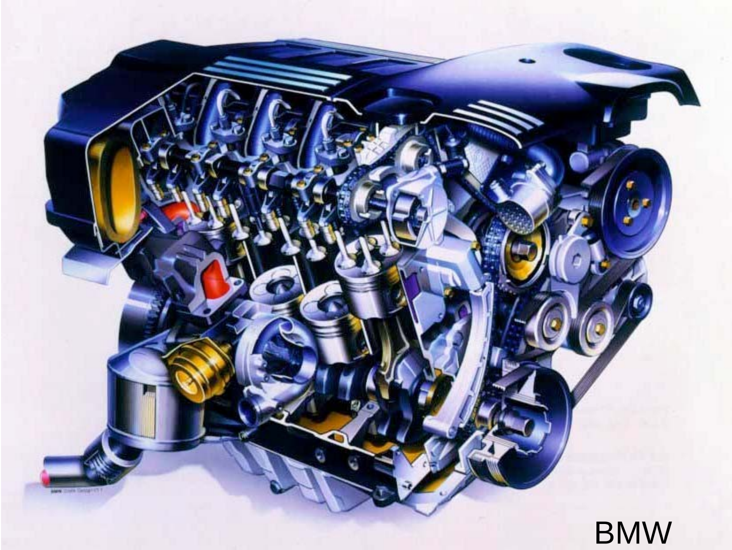


Objectives of research on immiscible alloys

- Industrial applications driven
  - Bearings in engines (cars, ships)
  - Electrical contacts
  - Composites

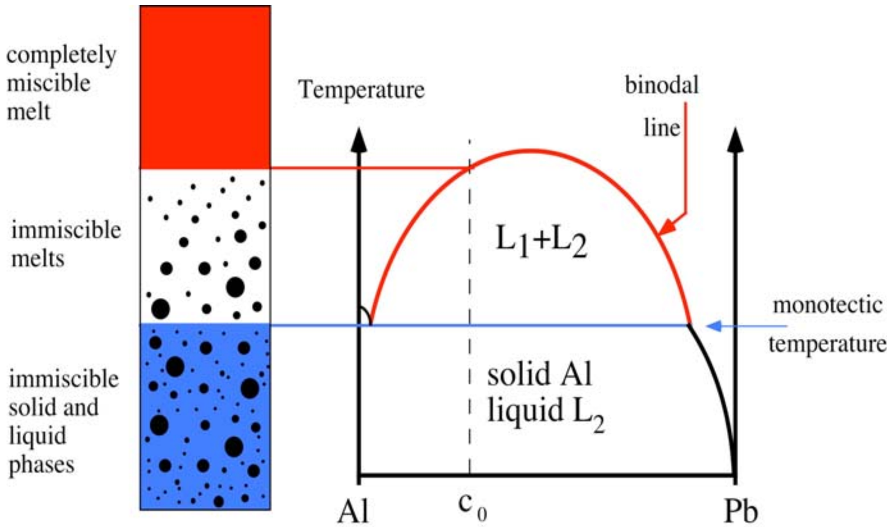
- Science driven
  - Numerous open problems in phase decomposition and spatial phase separation processes

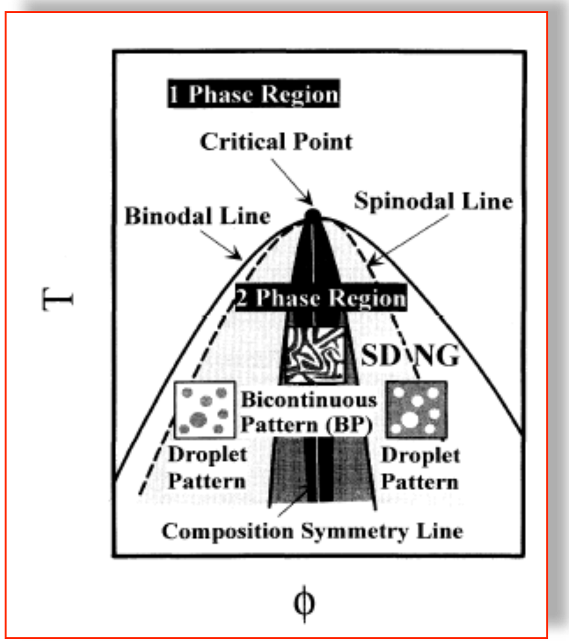
  Since
  - gravity leads to rapid sedimentation
  - fast liquid phase diffusion and precipitation


BMW


Zollern-BHW

Phase separation in immiscible monotectic alloys



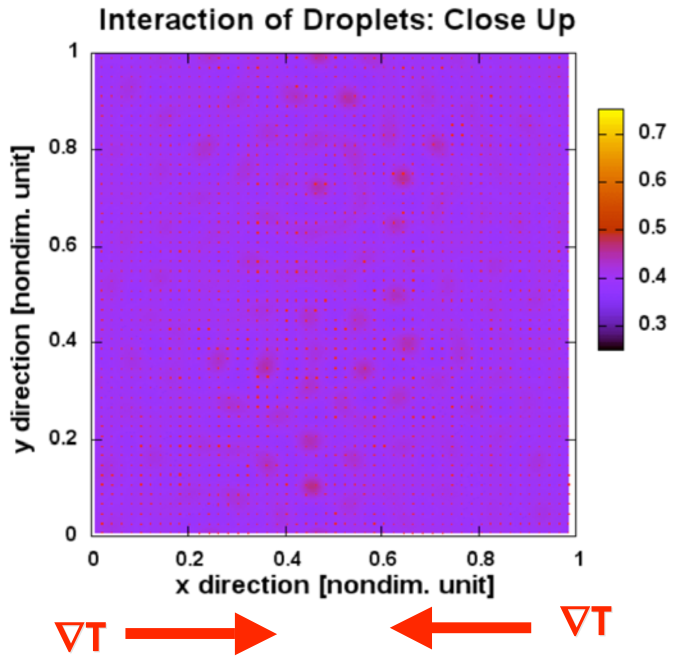


Some characteristic values

Temperature interval	$\Delta T = T_{bin} - T_{mon} = 0 - 300$ K
Typical cooling rates:	$dT/dt = 1 - 100$ K/s
Typical temperature gradients in solidification:	G= 1 - 10 K/mm
Length of two-phase zone	$l = \Delta T/G = 10 - 30$ mm
Time in miscibility gap	$t_s = \Delta T / dT/dt = 3 - 300$ s

Processes on passing the miscibility gap

- nucleation of drops of the minority phase
- growth in a supersaturated matrix
- Stokes-motion of drops (Sedimentation)
- Marangoni-motion of drops
- collision and coagulation of drops
- interaction of drops with the s/l interface
- natural convection
- monotectic reaction



Simulation for Al-Bi8

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Phase field simulation by G.Tegze & L.Granaszy, RISSPO, Budapest, Hungary

Multi-phase volume average model by M. Wu, A.Ludwig, Uni Leoben, Austria

Experimental approach

- Investigation of the phase separation processes with simple binary alloys like Al-Pb, Al-Bi and ternaries like Al-Pb-Bi

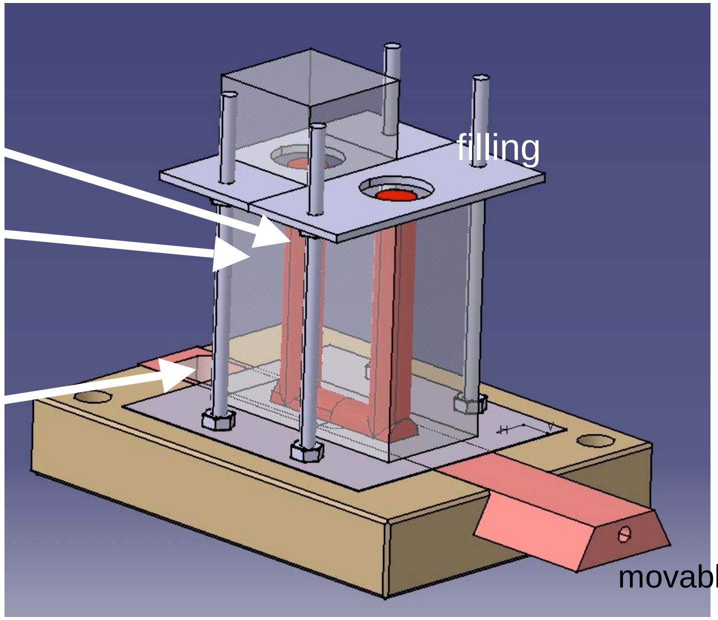
  Advantages:
  - established thermodynamics (free enthalpies)
  - established thermophysical properties (interfacial tension)

- Investigation of the effects of ternary alloying elements of industrial importance like
  Cu, Cr, Ni, Si, Sb, Zn, Mn, Fe, ...

  Advantages:
  at small amounts “binary” like miscibility gaps, but a variety of solidification front morphologies and the occurrence of a ternary eutectic reaction

Experimental methods

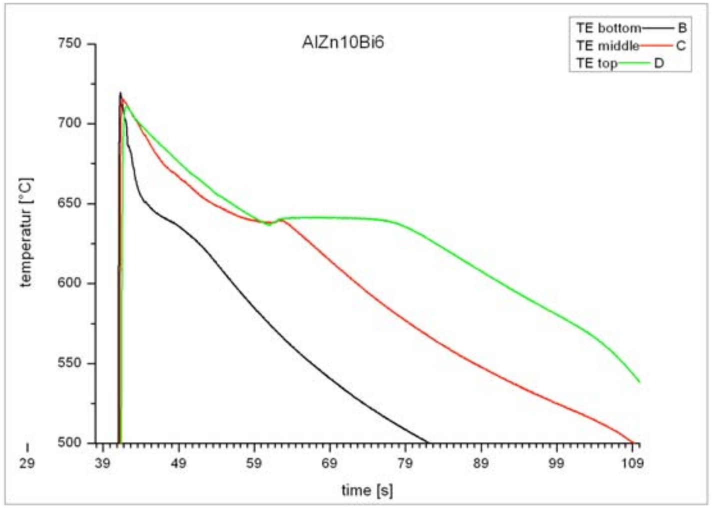
- Directional instationary solidification in aerogel moulds
- Radial solidification of cylindrical bars in moulds of various heat extraction conditions
- Experiments under microgravity conditions (no sedimentation and no natural convection)



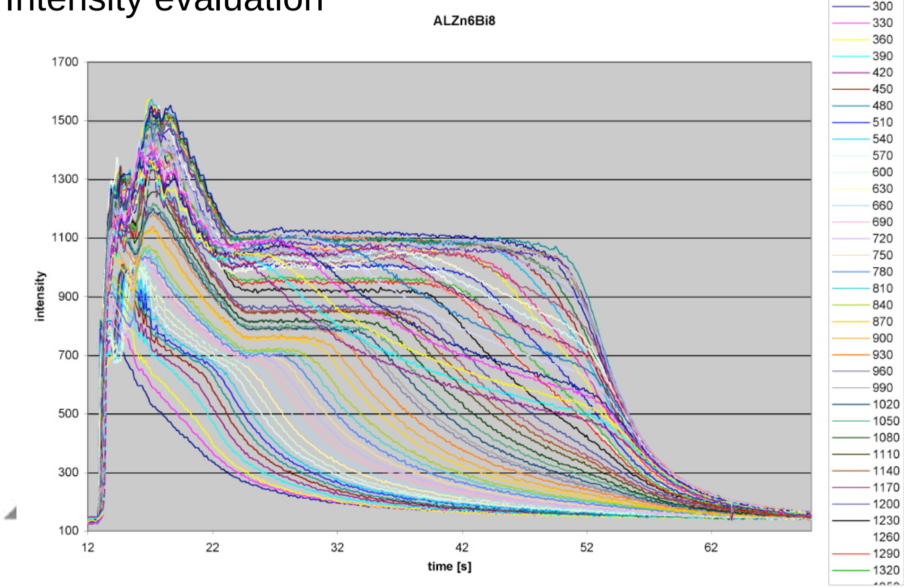
1. Counter Gravity Casting facility

- Filling of a cylindrical cavity from below (isolating aerogel mould)
- Initiating of cooling from below by moving a copper plate
- The solidification process is recorded optically with an IR-line CCD camera

Casting conditions in CGCF



- Thermocouple readings
- Intensity evaluation



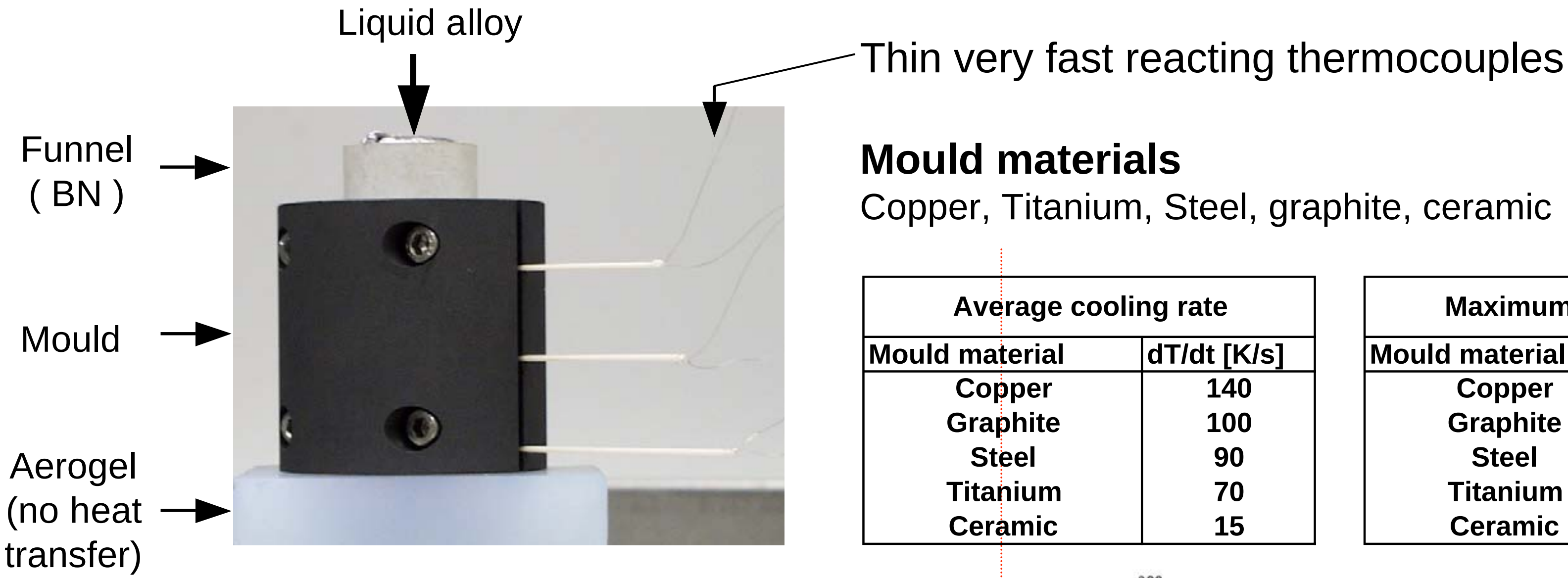
Alloy AlZn5Bi8+	Solidification velocity mm/s	
Cu2	1,04	
Cu2-TiB	0,91	
Cu2Sb0.5	0,74	
Cu2Sb0.5-TiB	0,52	
Cu2Sb1-TiB	0,92	
Cu2Sb5	2,4	Values from intensity recordings
Cu2Sb5-TiB	0,42	
Cu2Ni0.5	1,13	
Cu2Ni0.5-TiB	0,76	
Cu2Ni1	0,76	
Cu2Ni1-TiB	1	
Cu4	1,16	
Cu4-TiB	0,8	
Zn6Bi8Si5	0,6	
Average	**0,94**	

Average cooling rate in the miscibility gap

T_{top}= 3.9 K/s
T_{middle}= 4.1 K/s
T_{bottom}= 15.2 K/s

Average gradient: G=40 K/cm

2. Casting into permanent moulds

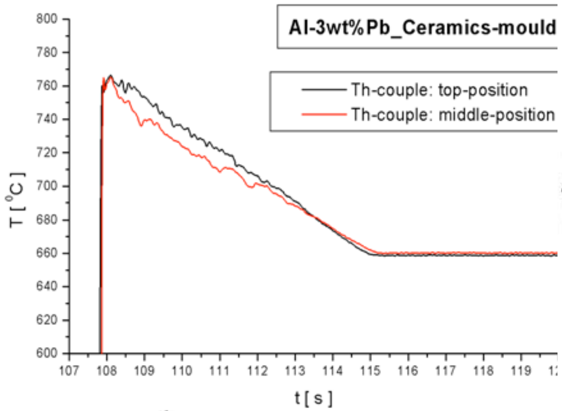


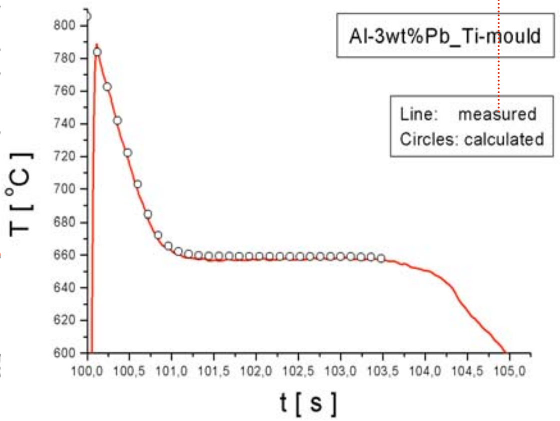
Mould materials

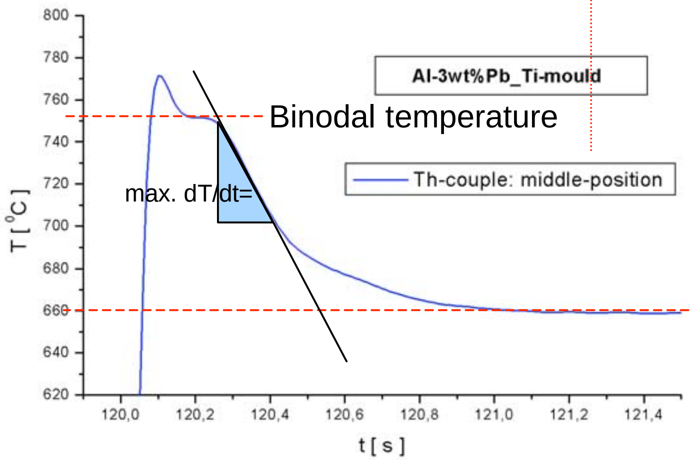
Copper, Titanium, Steel, graphite, ceramic

Average cooling rate	
Mould material	**dT/dt [K/s]**
Copper	**140**
Graphite	**100**
Steel	**90**
Titanium	**70**
Ceramic	**15**

Maximum cooling rate	
Mould material	**dT/dt [K/s]**
Copper	**1050**
Graphite	**280**
Steel	**809**
Titanium	**233**
Ceramic	**25**



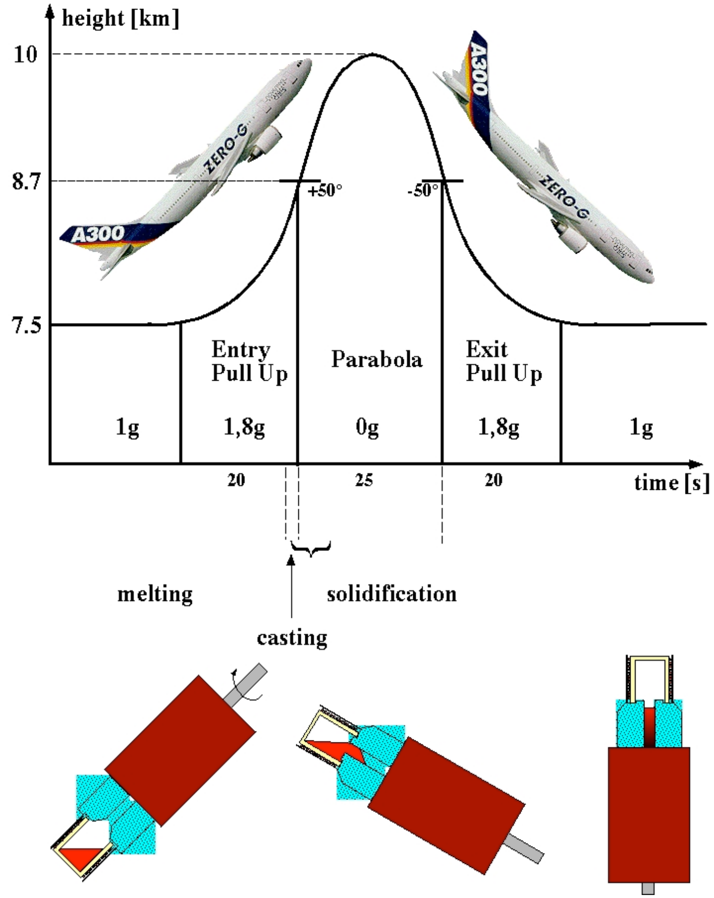




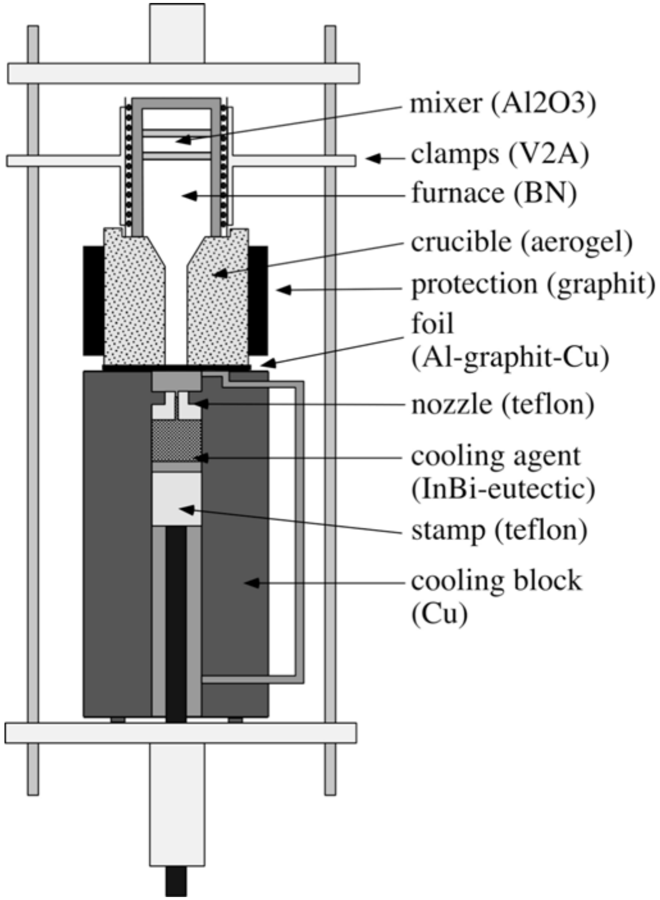
3. Parabolic flights - Microgravity for 20 seconds

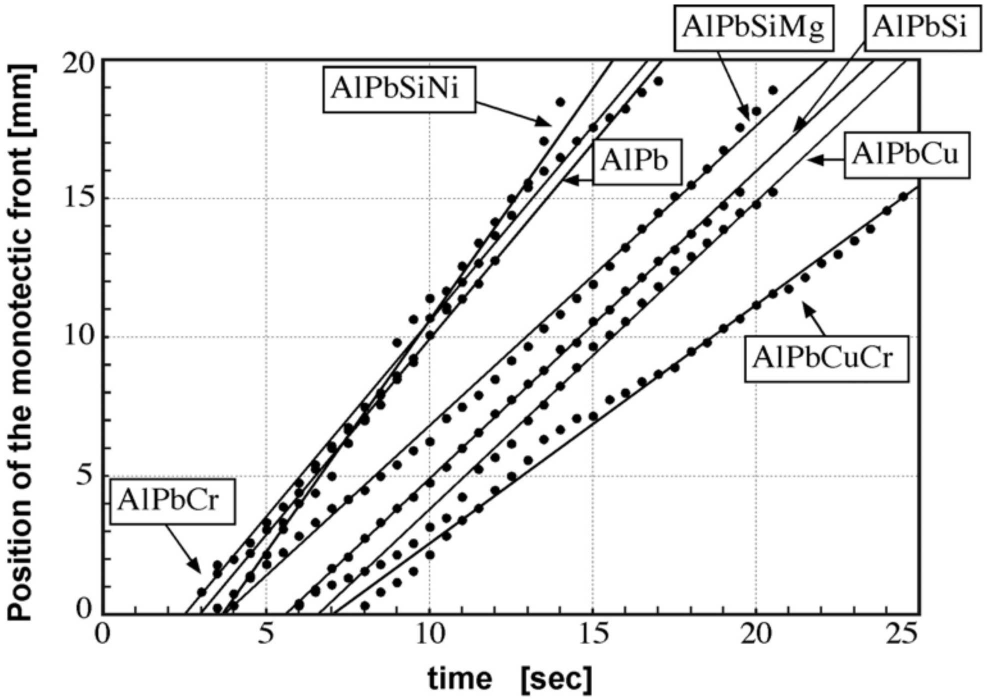
casting during 1-g or 2-g phase into a suitable mould

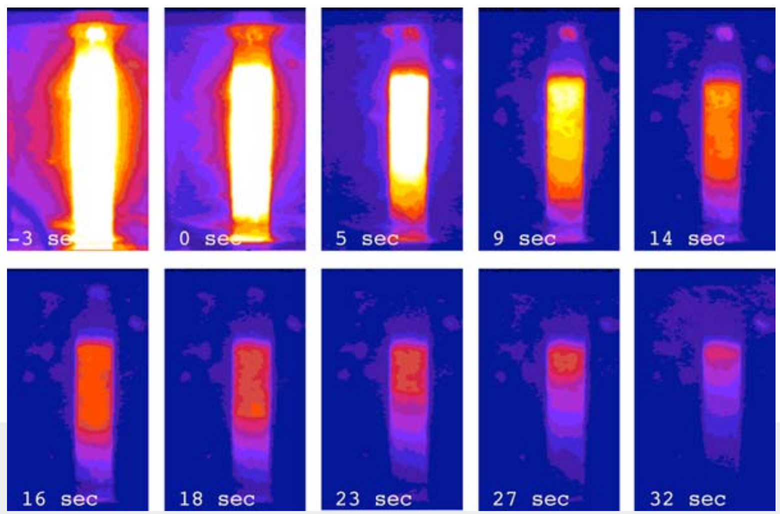
- start of cooling at the onset of microgravity
- alloy homogenization with stirring
- directional solidification in quasi-adiabatic moulds (aerogels)
- optical measurement of the temperature profile
  - measurement of solidification velocity
  - measurement of temperature gradient
  - large number of samples per flight campaign



Aerocast - casting in microgravity



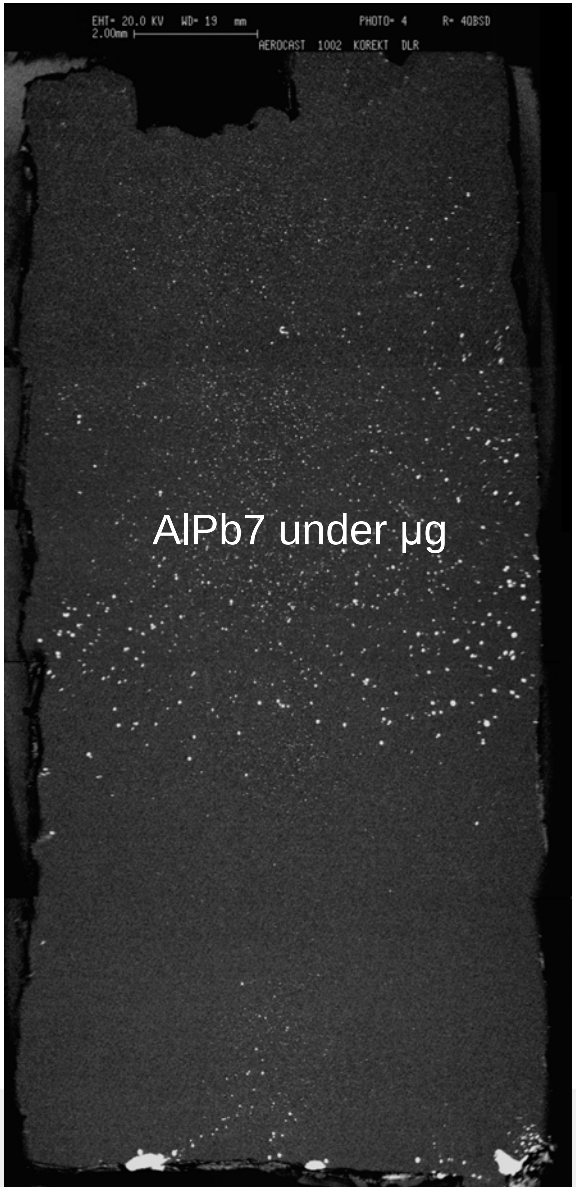


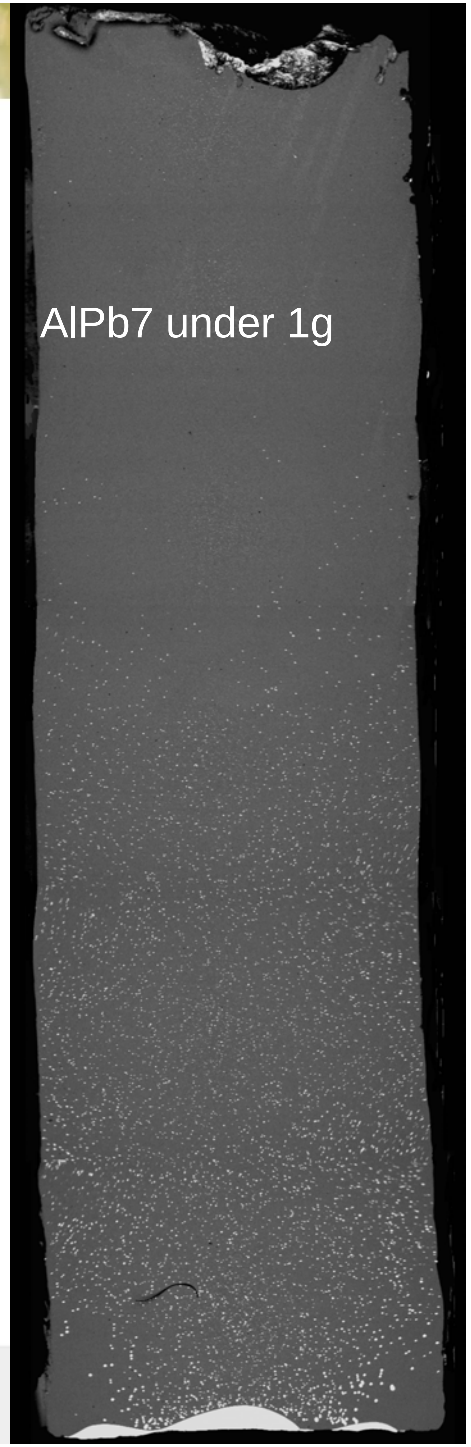


the casting device

Experiments performed under µg

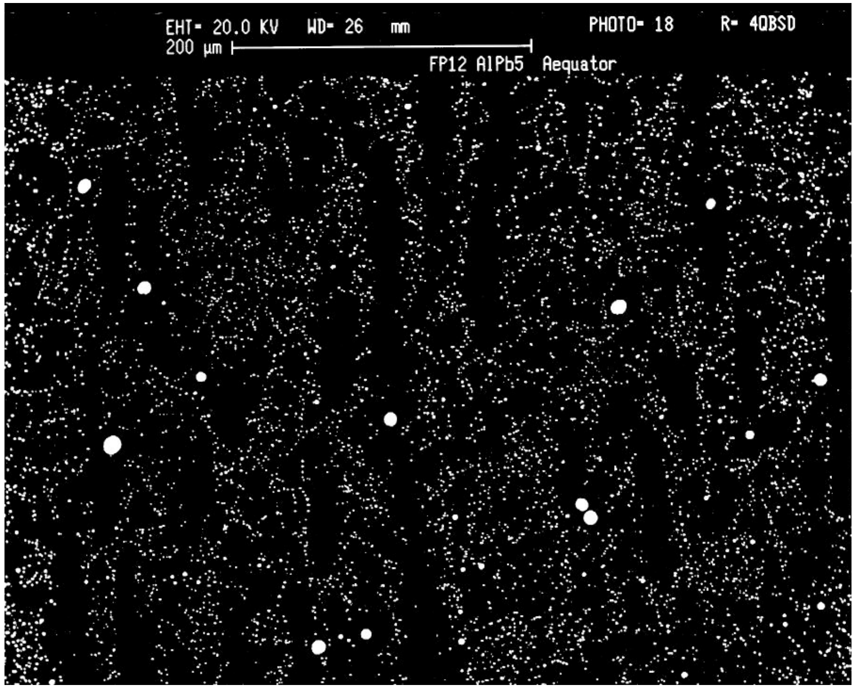
- Parabolic flights in
  1995, 1997,1998,
  1999, 2000,2006
- Alloys studied
  - Al-Bi (5 -15 wt%)
  - Al-Pb-Bi
  - Al-Pb7 with
    - Si (3.5 & 7 wt.%)
    - Cr (0.1 wt.%)
    - Cu (3 wt.%)
    - Si & Ni (1 wt.%)
    - Cu & Cr
  - Al-Zn-Bi



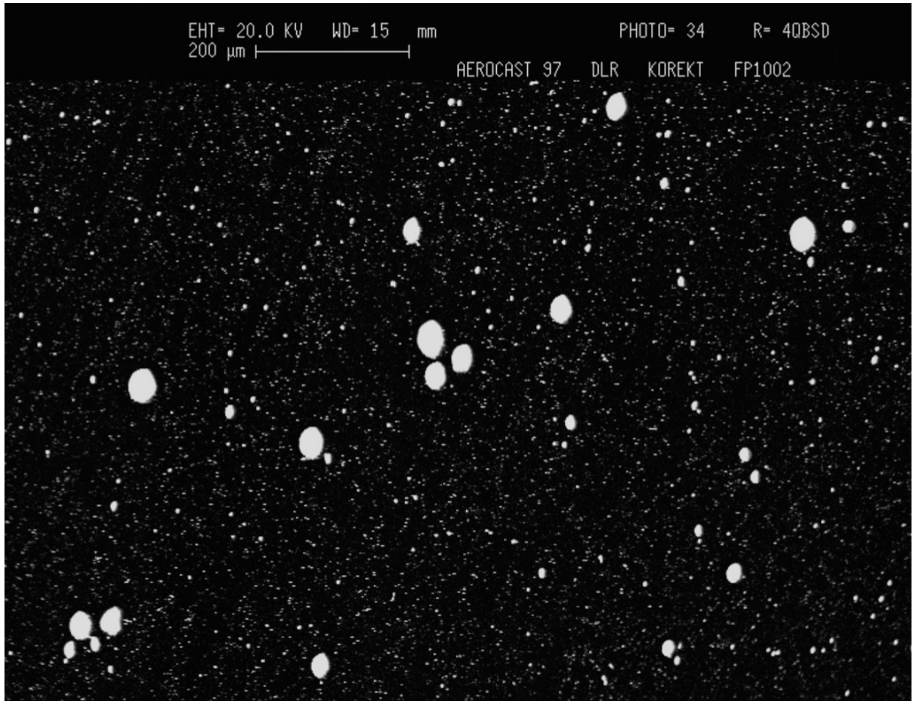


Experimental results on binary alloys

Casting and solidification under 1g and µg in aerogels
pure binary alloys



Al-5 wt.% Pb

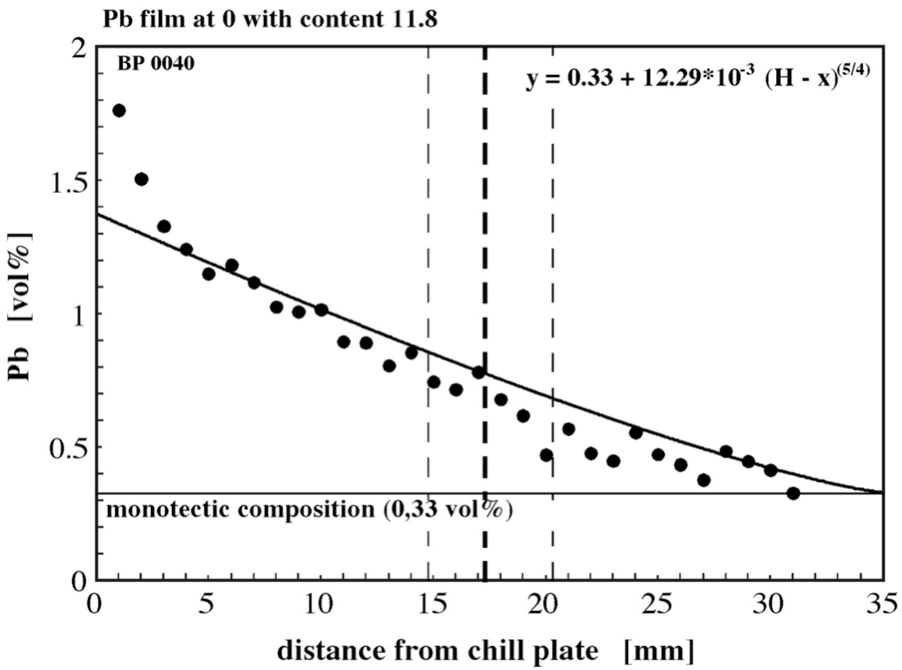


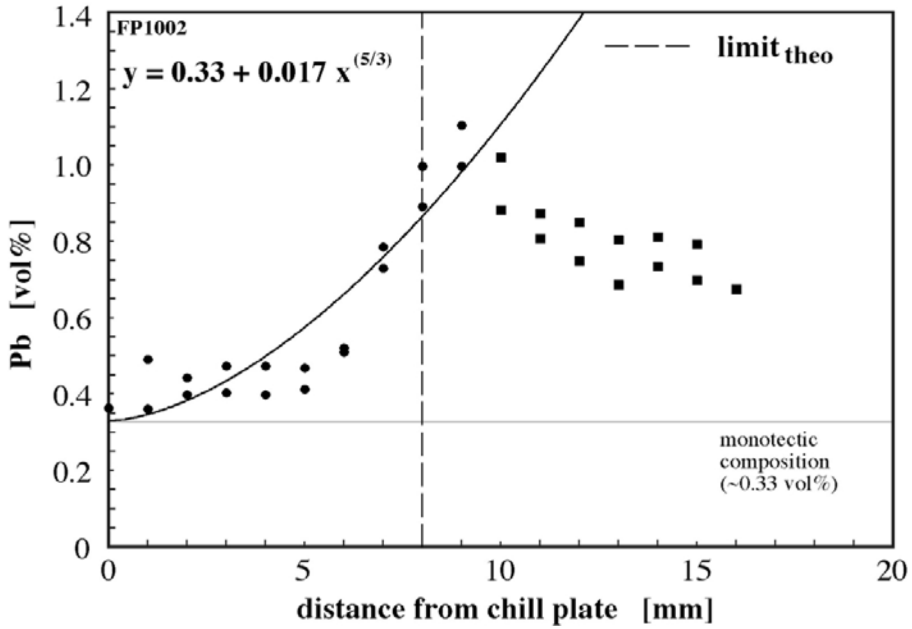
Al-7 wt.% Pb

Casting and solidification under 1g and µg in aerogels

volume fraction distribution in samples

alloys Al-7 wt.% Pb





Theory:
Time-space evolution of liquid precipitates due to nucleation, drop motion and growth

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial z}\left(u(R,z)\,f\right) + \frac{\partial}{\partial R}\left(\frac{dR}{dt}\,f\right) = \left.\frac{\partial I(R,z,t)}{\partial R}\right|_{R=R^*}$$

$$\Phi(t) = \int_0^\infty R^3 f(R,t)\,dR \qquad f(R,z,t) = \text{drop size distribution}$$

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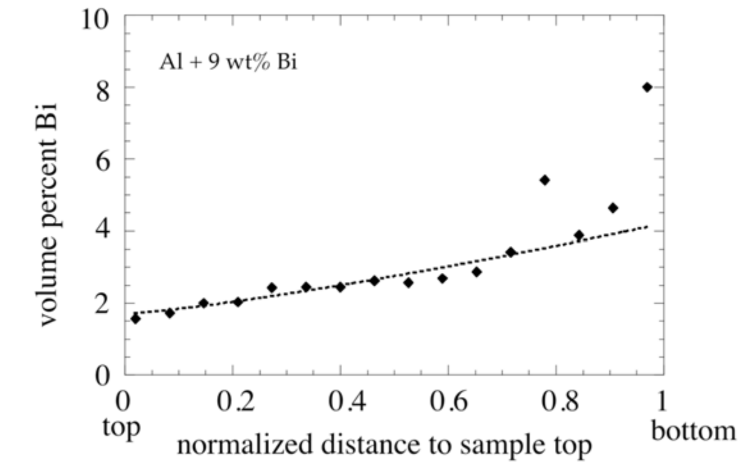
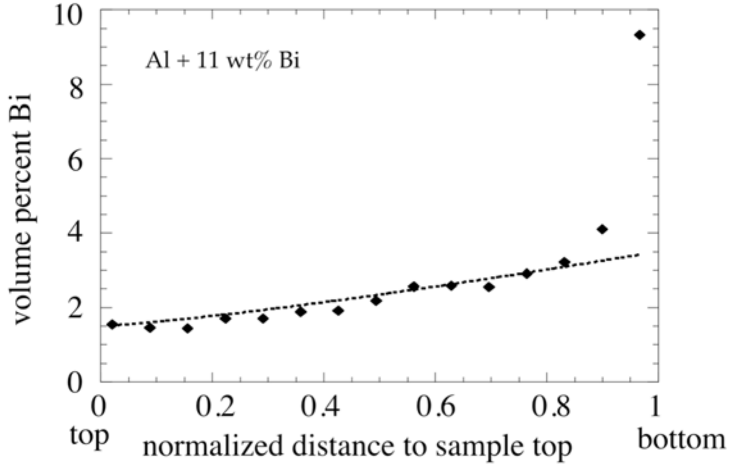
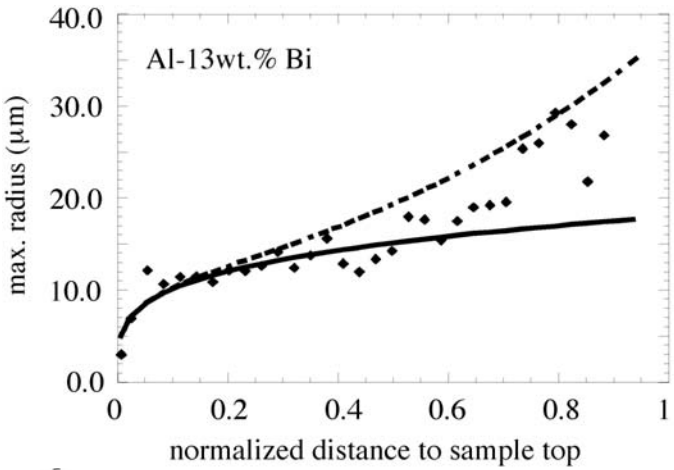
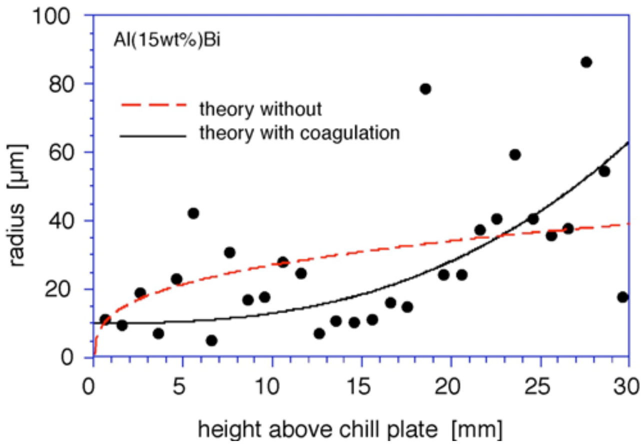
Casting and solidification under 1g conditions

volume fraction distribution in binary AlBi alloys







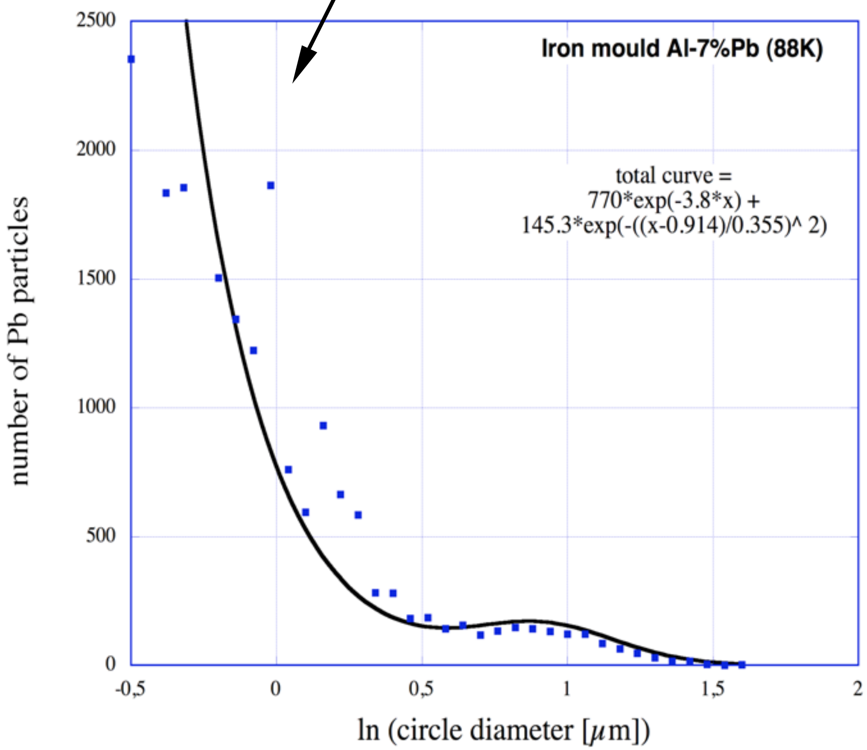


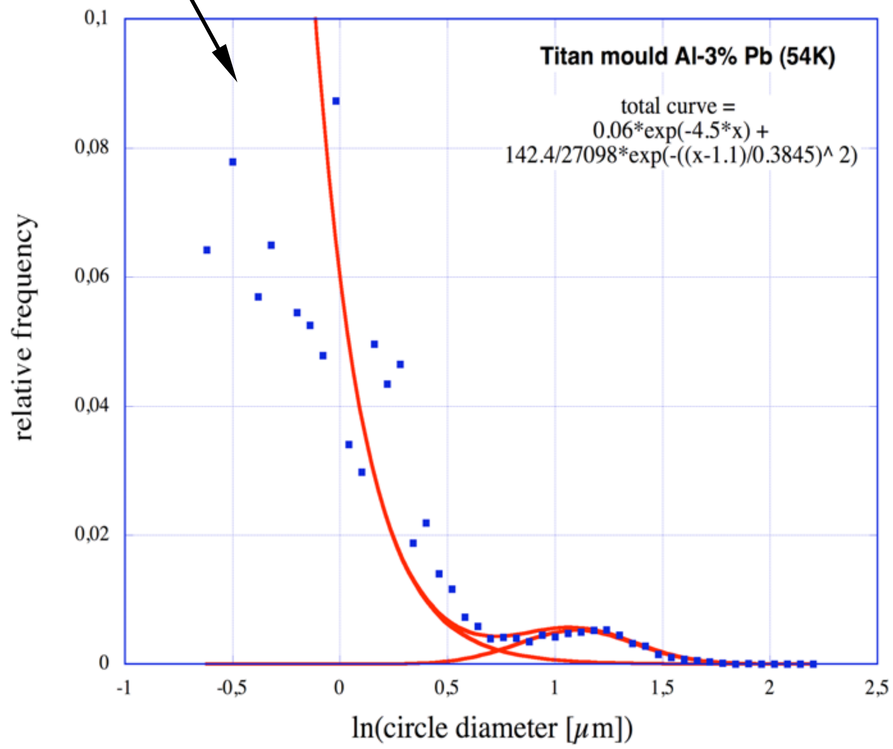
Parabolic flight result

Laboratory results on AlBi alloys cast into an aluminium oxide mould cooling from below

Particle size distributions and particle size separation

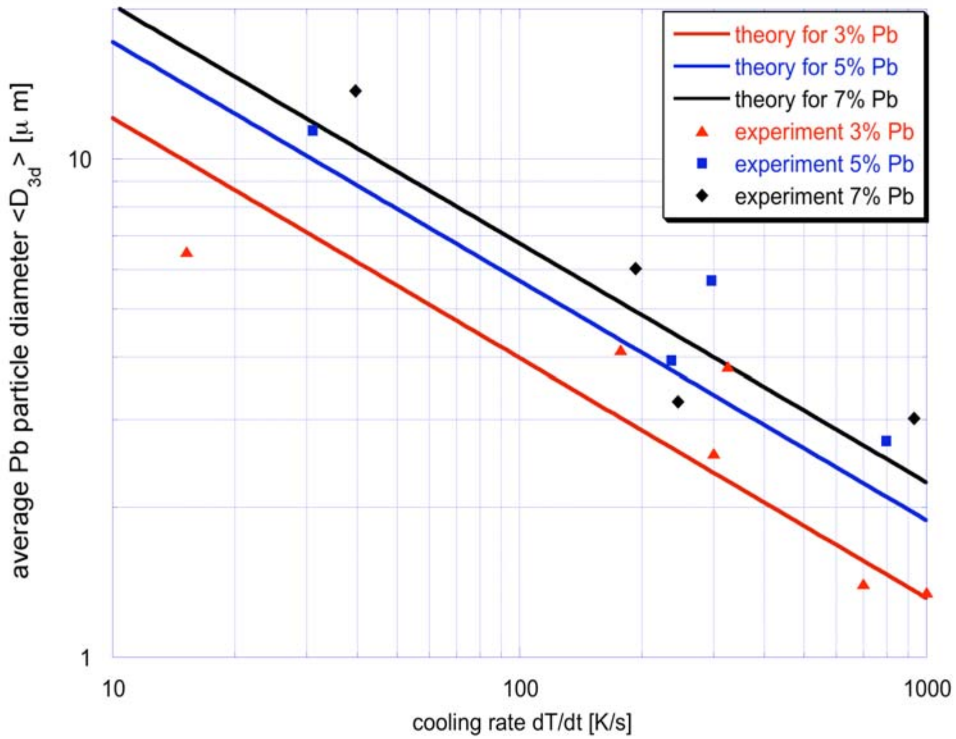
Small particles created by monotectic reaction





Large particles nucleated and grown on passing the miscibility gap

Results of cooling rate experiments



Nucleation shall be homogeneous nucleation (Ratke&Uebber 1990, Granasy&Ratke1996)

$$I = I_0 \exp[-\frac{\Delta G_c}{k_B T}]$$ nucleation rate

$$I_0 = \frac{24 n_c^{2/3} D}{(X_A \Omega_A + X_B \Omega_B)\lambda} \left(\frac{\Delta G_c}{3\pi k_B T n_c^2} \right)^{1/2}$$

$$\Delta G_c = \frac{16}{3} \pi \frac{\sigma^3}{\Delta G_v^2}$$ nucleation barrier

- ΔG_v from phase diagram and thermodynamics !
- Interface tension for Al-base alloys are well determined by the group of Hoyer, Chemnitz

$$\sigma_{L1L2}(T) = \sigma_0 \left(1 - \frac{T}{T_c} \right)^{1.5}$$

growth rate $$\frac{dR}{dt} = D \frac{C_m(R,t) - C_I(R,t)}{C_{L2}(t) - C_I(R,t)} \frac{1}{R}$$

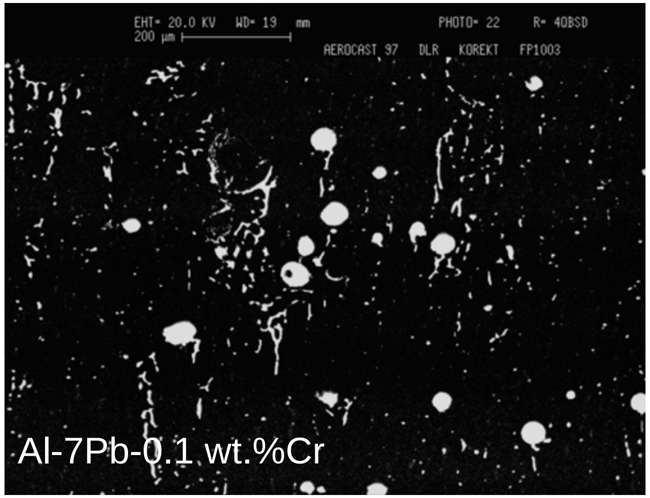
growth rate with interface concentration $$C_I(R,t) = C_m^\infty(t) \exp\left(\frac{2\sigma \, \Omega_d}{k_B T \, R} \right)$$

Theoretical prediction $$\langle D_{3d} \rangle \propto \left(\frac{T_{bin} - T_{mon}}{dT/dt} \right)^q$$ 0.45 < q ≤ 1/2

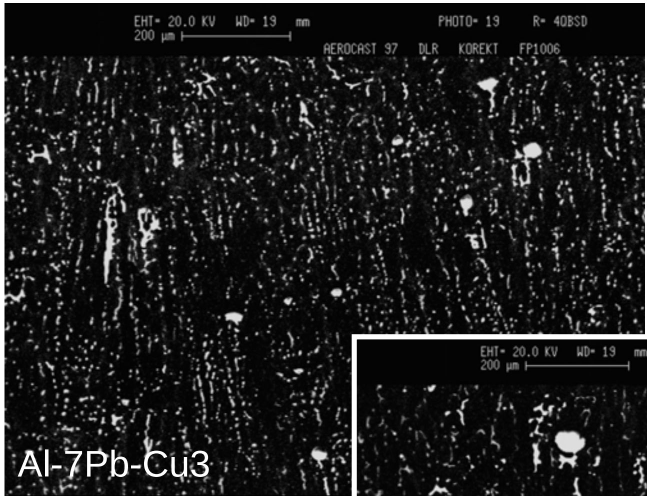
Experimental results on ternary alloys

Casting and solidification under µg

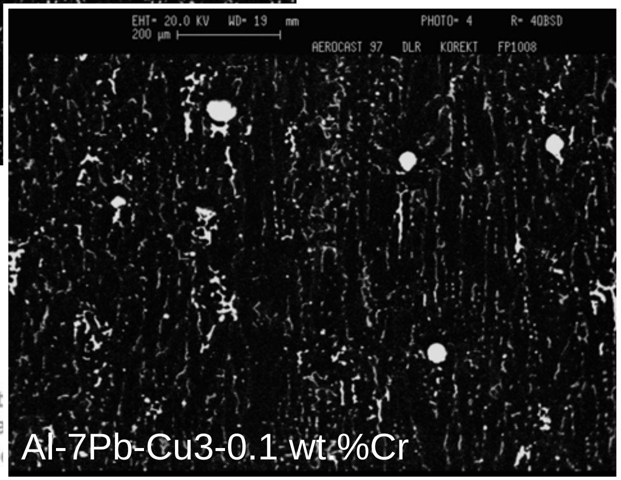
effect of alloying



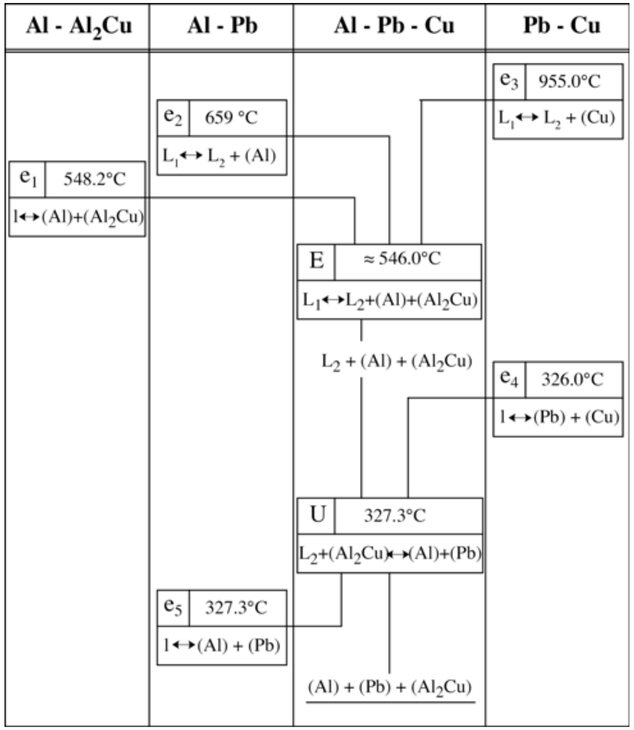
Al-7Pb-0.1 wt.%Cr



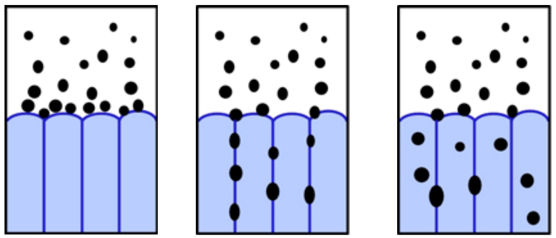
Al-7Pb-Cu3



Al-7Pb-Cu3-0.1 wt.%Cr



Drop pushing, entrapment, engulfment



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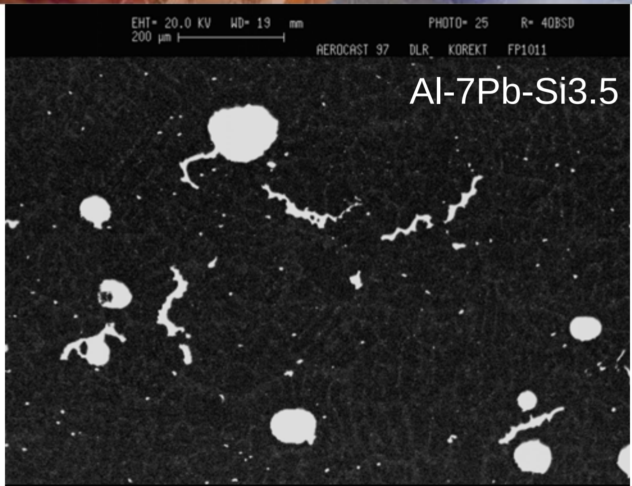
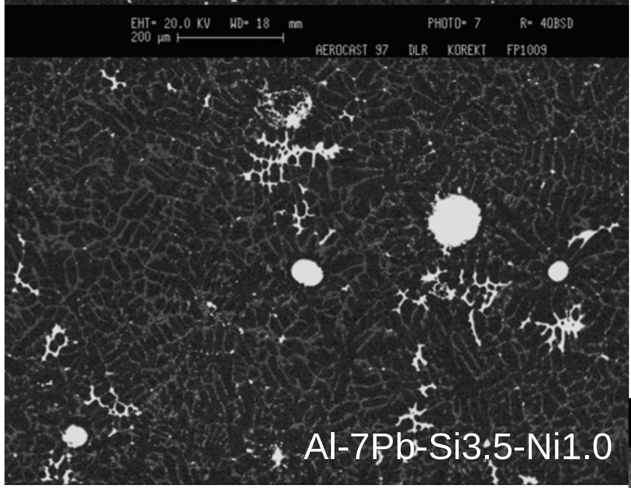
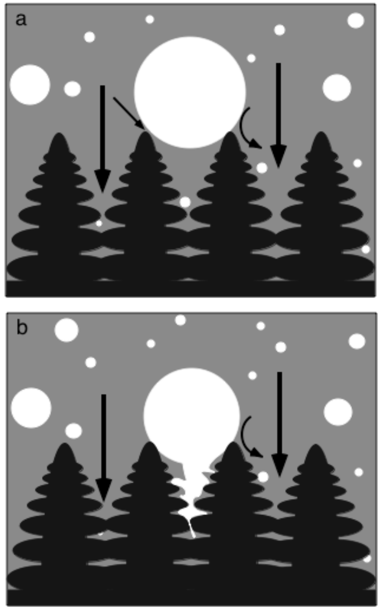
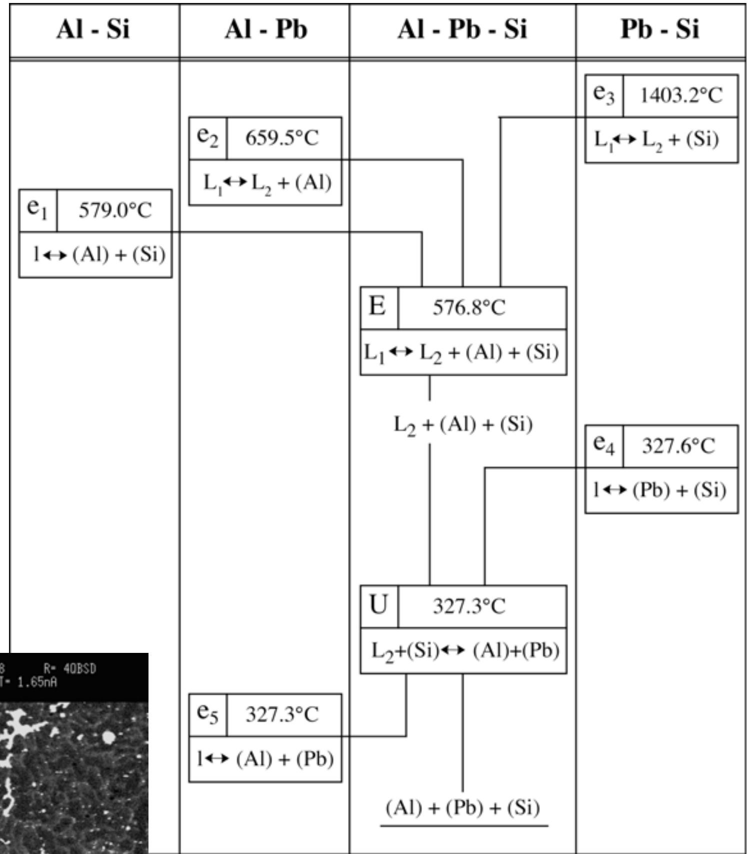
Casting and solidification under µg

effect of alloying

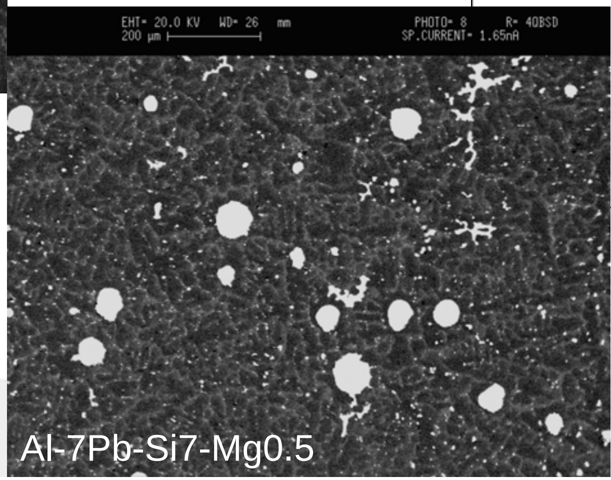






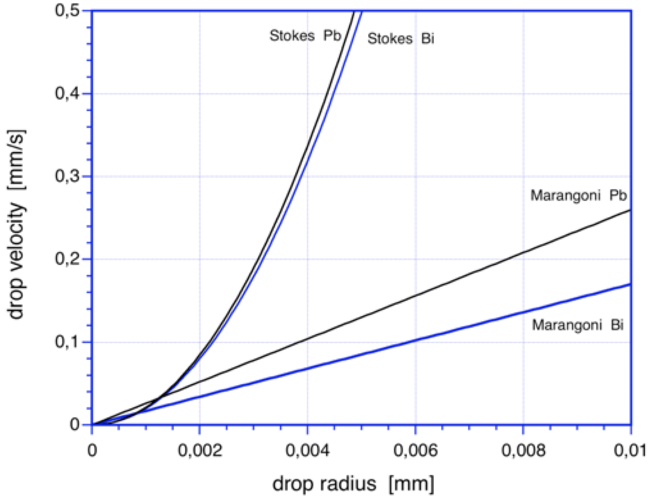


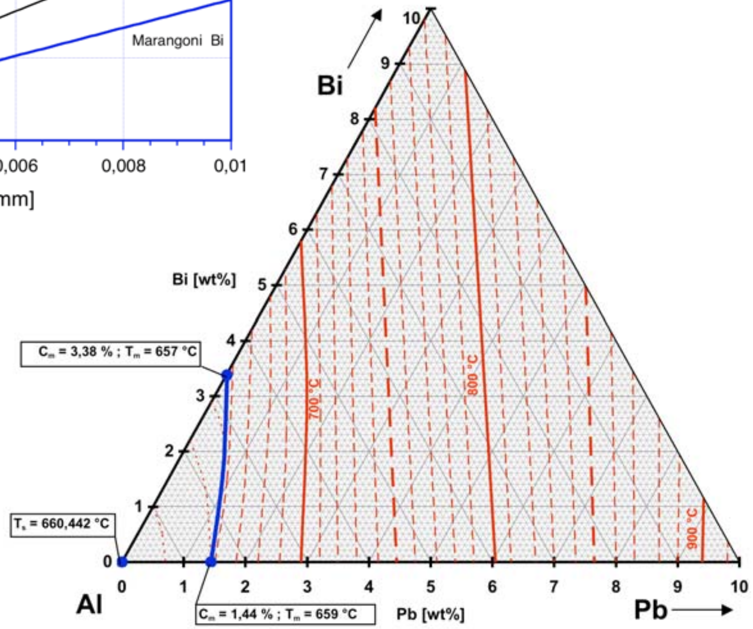
after Sommer and Yu

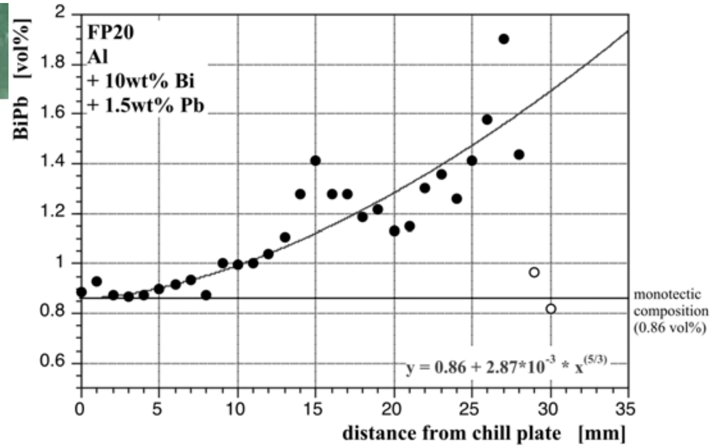


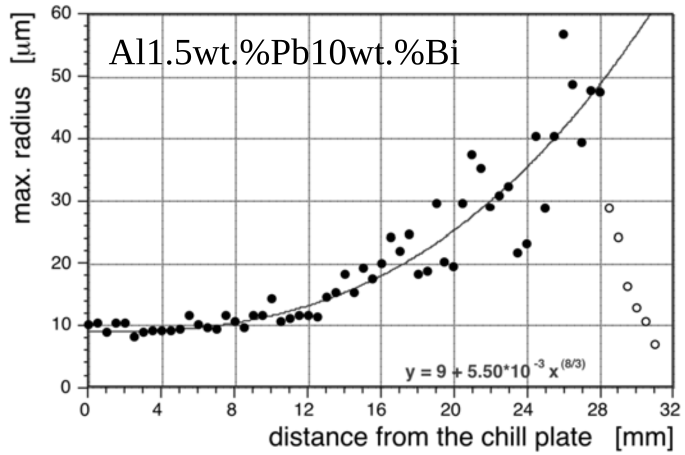
Al-Pb-Bi under microgravity

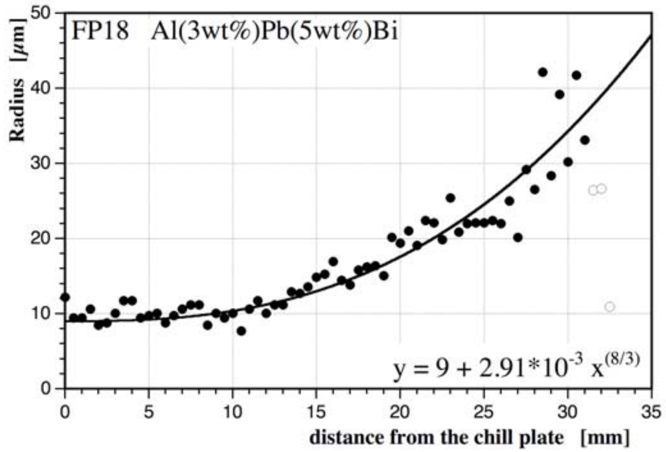
Idea:Continuous variation of interfacial tension going from Al-Pb (125.5 mJ/m²) to Al-Bi (57 mJ/m²) and thus different Marangoni velocities.











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After Sommer private communications

A new multi-component bearing material based on AlZnBi

Alloys investigated

Base alloy

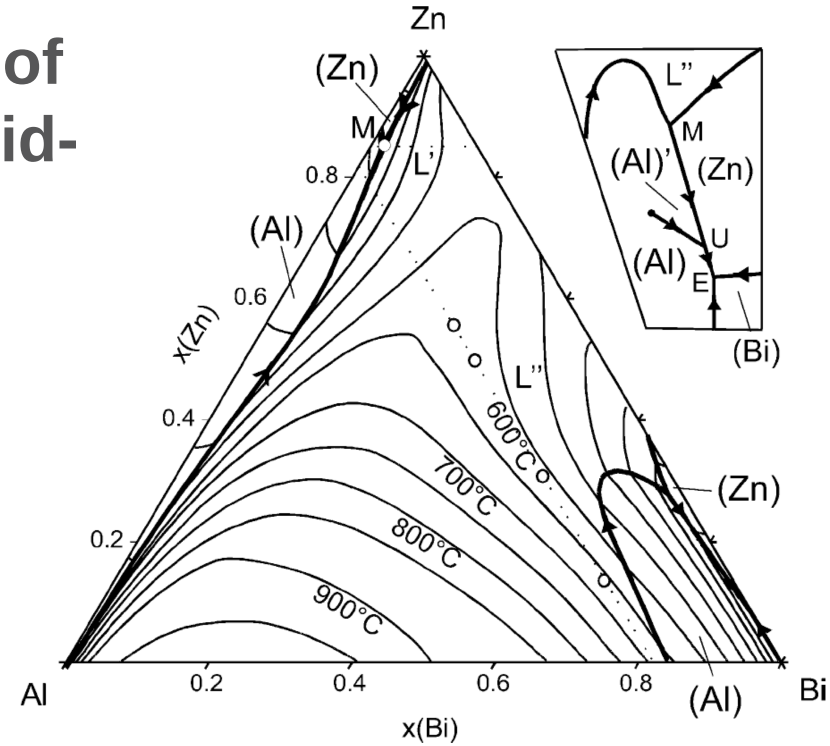
$AlZn_{5-12}Bi_{5-10}$

- Cu for age hardening
- Sb to reduce corrosion of Bi
- Ni, Si, Cr, Ta,
- TiB_2 as a grain refiner

all values in weight percent

No	**Zn**	**Bi**	**Cu**	**Sb**	**Ni**	**Si**	**TiB**
1	5	8	2	0,5			
2	5	8	2	0,5			y
3	5	8	2	1			
4	5	8	2	1			y
5	5	8	2	5			
6	5	8	2	5			y
7	5	8	4				
8	5	8	4				y
9	5	8			0,5		y
10	5	8			0,5		
11	5	8	2		0,5		
12	5	8	2		0,5		y
13	5	8			1		y
14	5	8	2		1		
15	5	8	2		1		y
16	5	8	2	1,7			
17	5	8		5			
18	5	8		5			y
19	5	8		1			y
20	5	8		1,7			y
21	5	8	2				
22	5	8	2				y
23	5	8		0,5			y
24	5	8		0,5			
25	6	5					
26	6	7					
27	6	8				5	
28	8	5					
29	8	7					
30	10	5					
31	10	7					
32	12	5					
33	12	7					

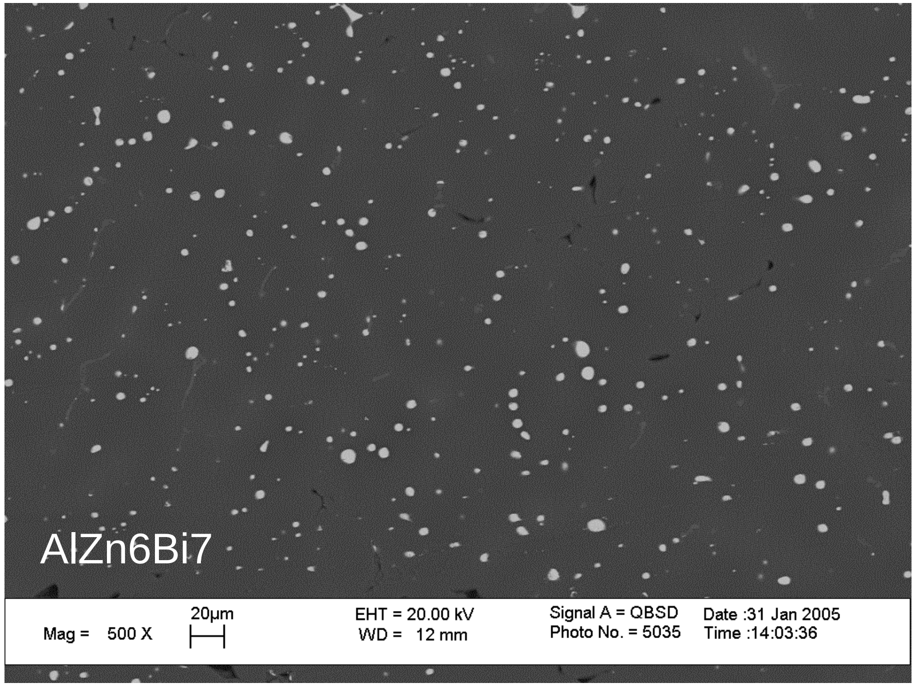
Thermodynamic assessment of AlZnBi by Gröbner and Schmid-Fetzer



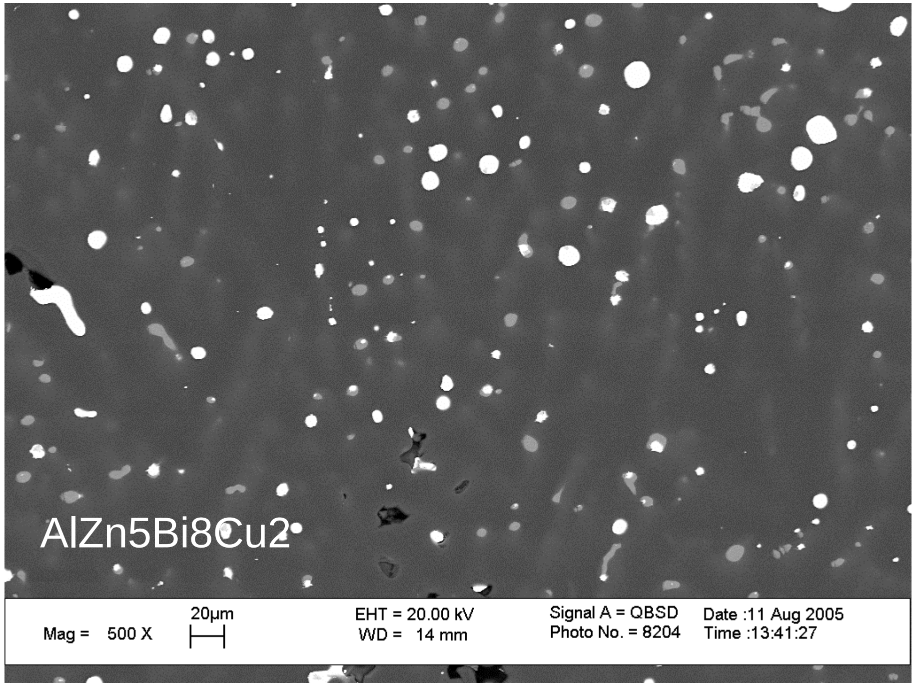
Calculated invariant reactions with composition of the phases

Reaction	T (°C)	Type	Phase	at.% Al	at.% Bi	at.% Zn
L′ = L″ + (Al)′ + (Zn)	376.1	M	L′	12.67	1.64	85.69
			L″	2.09	70.52	27.39
			(Al)′	33.16	0.05	66.79
			(Zn)	3.01	0.33	96.66
(Al)′ + L″ = (Al) + (Zn)	278.1	U	(Al)′	41.07	0.02	58.91
			(Zn)	1.61	0.17	98.22
			(Al)	85.78	≈0.002	14.22
			L″	0.55	89.31	10.14
L″ = (Zn) + (Al) + (Bi)	253.9	E	L″	0.38	91.58	8.04
			(Zn)	1.25	0.14	98.61
			(Al)	89.51	≈0.001	10.49
			(Bi)	–	98.39	1.61

Microstructures



L_2-drops at grain boundaries and in the volume

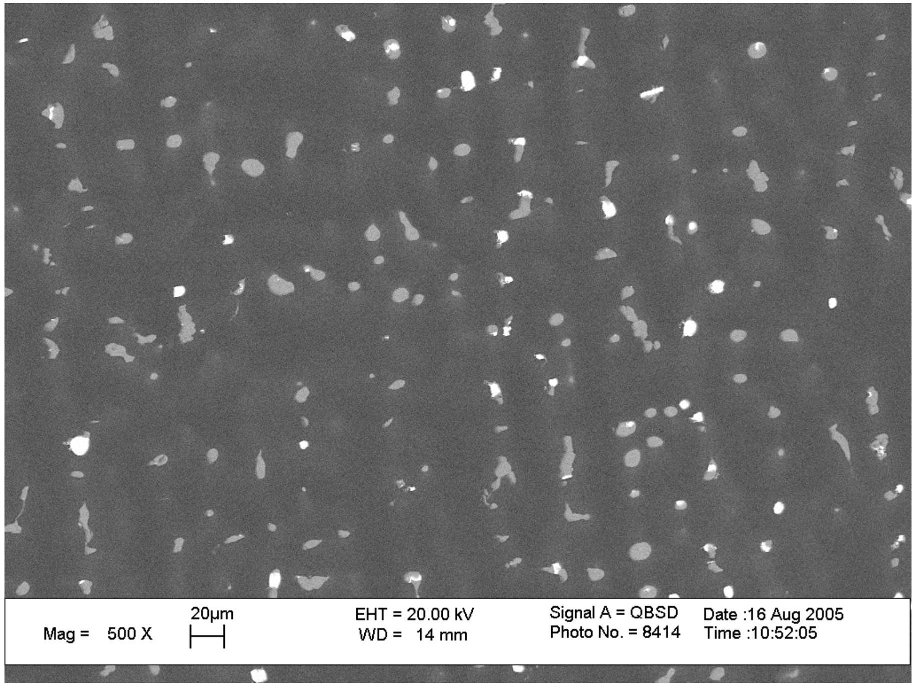


L_2-drops at grain boundaries and in the volume; non-equlibrium Al_2Cu-eutectic at grain boundaries associated with Bi-drops

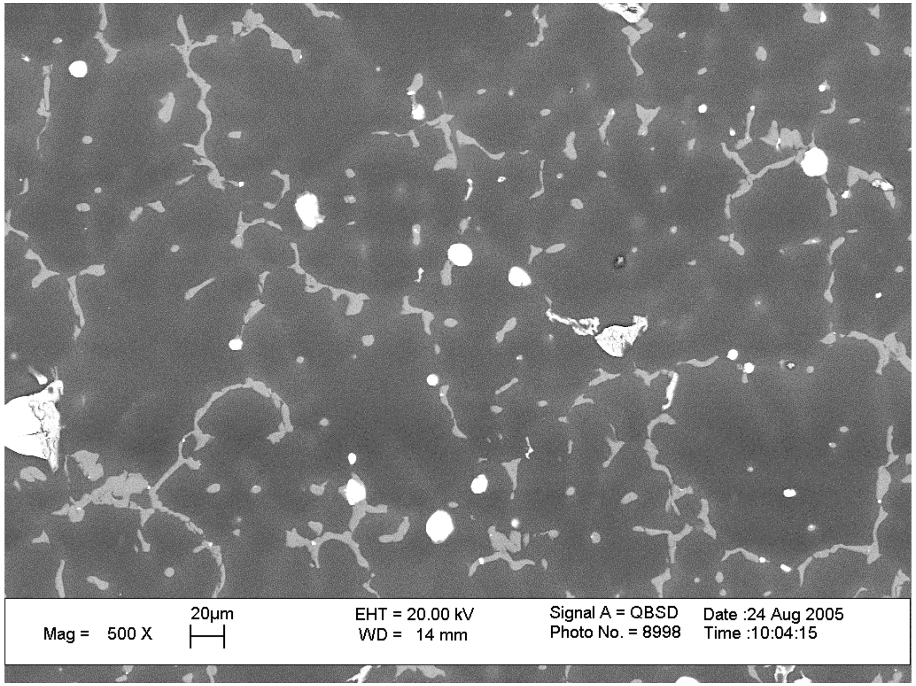
Microstructures

- more copper: AlZn5Bi8Cu4

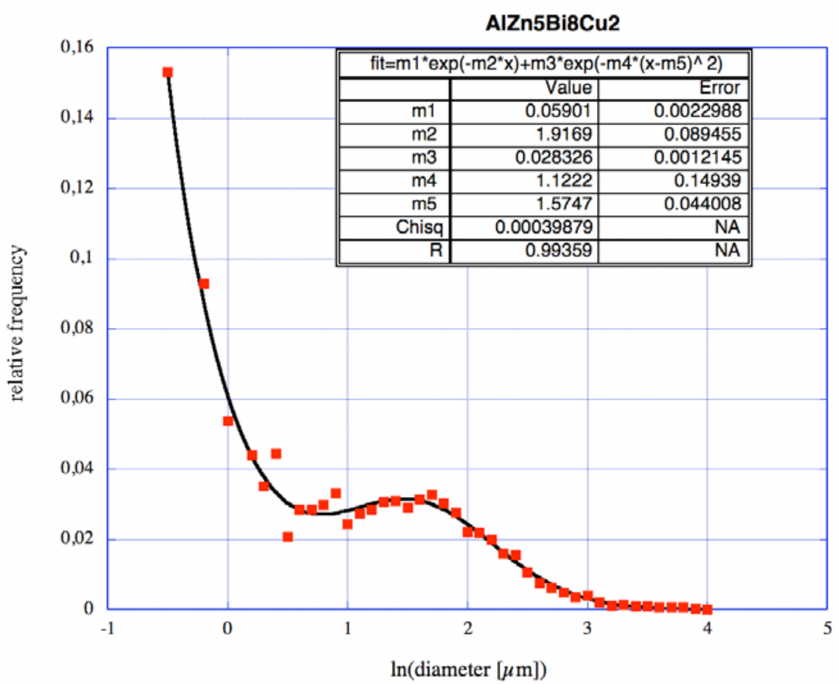
without

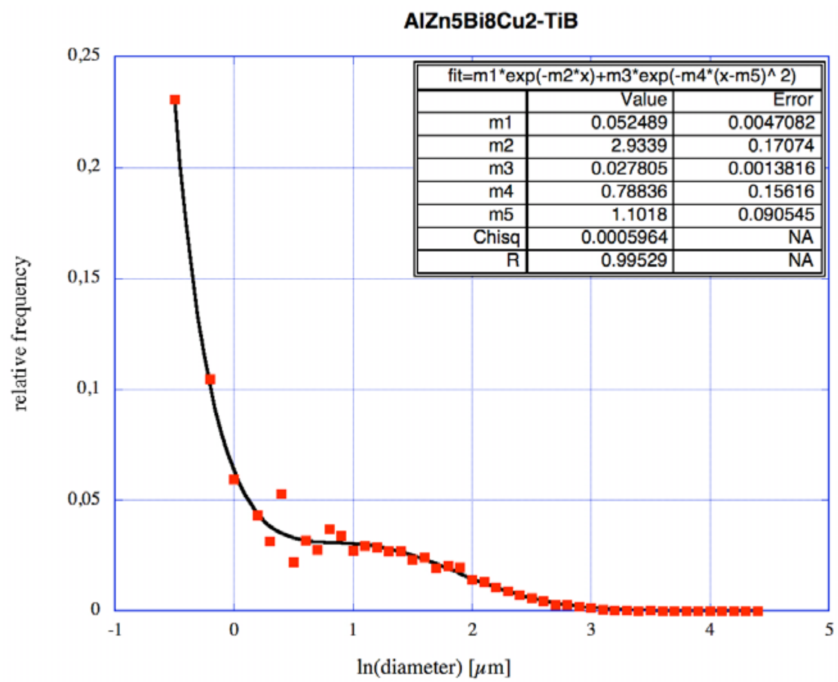


and with TiB_2



Size distributions



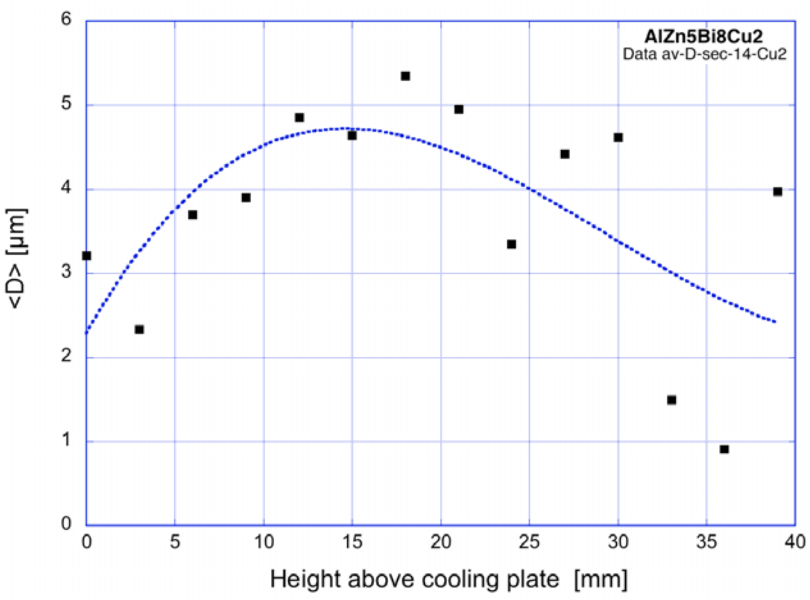


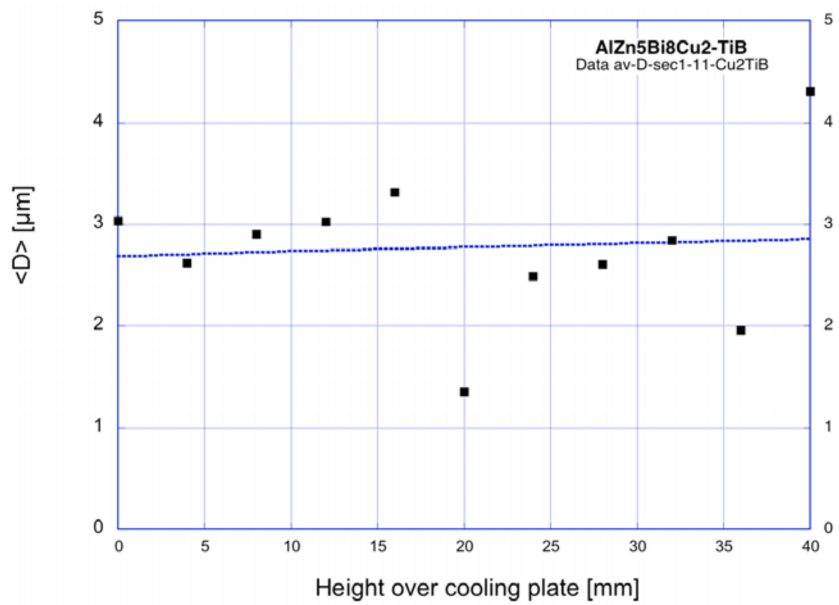
Separation of the particles stemming from the

- Monotectic reaction (small ones)
- Cooling through the miscibility gap (larger ones)

Miscibility gap particles are modelled as log-normal distributions

Average Bi droplet sizes





Variation of drop diameter with position:

Solutal Marangoni motion in ternary alloys is stronger than Stokes motion?!

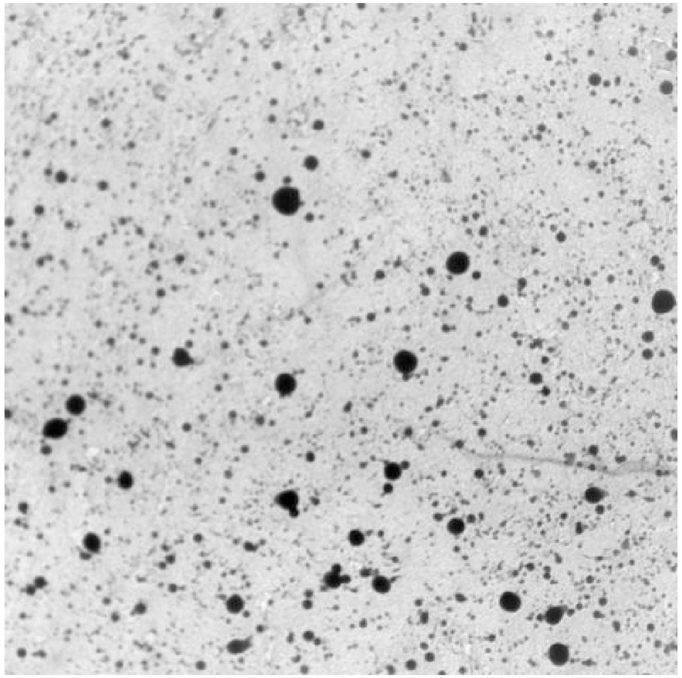
no variation with a grain refiner:

Nucleated equi-axed growth along the univariant monotectic reaction line impedes segregation of Bi.

Bi drop size of only those drops stemming from the miscibility gap

Summary and Outlook

- Quantitative understanding of liquid-liquid decomposition lacking
- Thermodynamics of multi-component alloys and solidification paths are essential as well as thermophysical properties



Schaffer, Mathiessen, Arnberg
New Journal of Physics 2008

Future

- 3D analysis of samples using x-ray tomography
- solidification experiments with in-situ observation by synchrotron radiation