INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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SMR/382- 43

WORKSHOP ON SPACE PHYSICS:
"Materials in Micorgravity"
27 February - 17 March 1989

"Alloys and Composites"

H.J. SPRENGER
INTOSPACE
Hannover
Federal Republic of Germany

Workshop on Space Physics
Materials in Microgravity

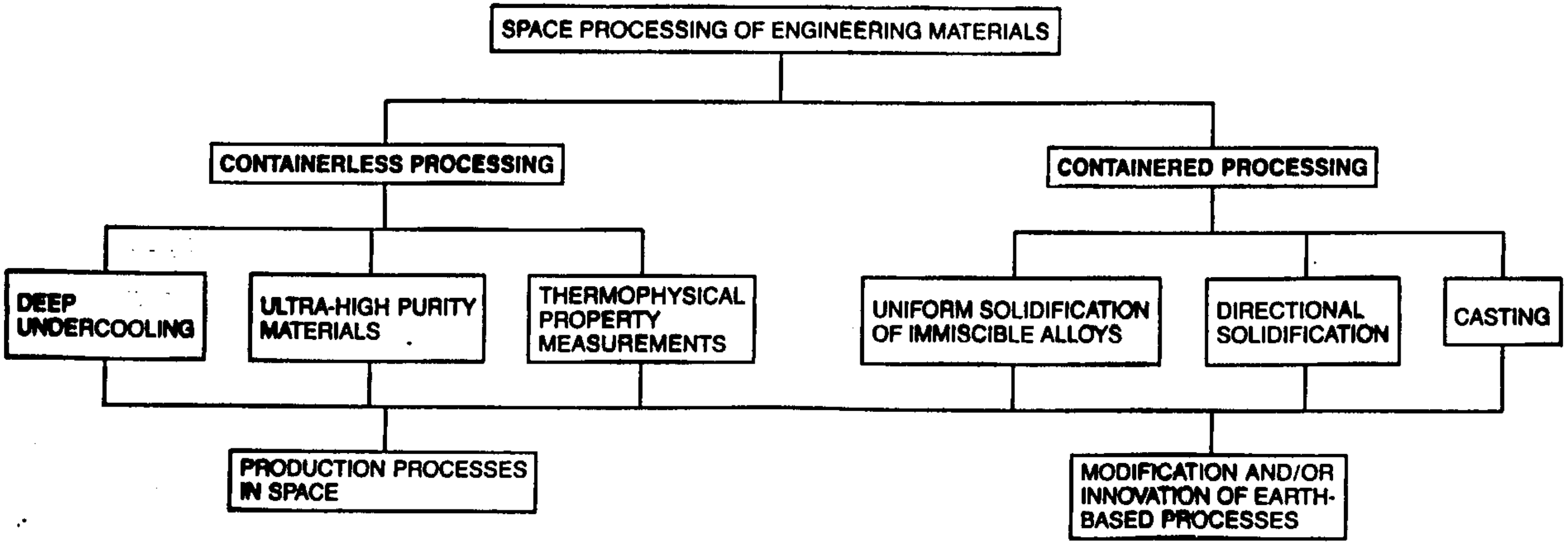
"ALLOYS AND COMPOSITES"

Heinz J. Sprenger
INTOSPACE, Hannover, FRG

International Centre for Theoretical Physics
Trieste, Italy
February 27 - 17 March, 1989

Contents:

SPACE PROCESSING ACTIVITIES



Processes of interest

- Casting of single or multiphase alloys (containered processes)

  * Directional solidification studies
  Planar front growth (macrosegregation)
  Dendritic growth (microsegregation)
  Diffusion at an advancing solidification front
  Undercooling due to solute redistribution

  * Eutectic growth
  Influence of convection on the microstructure
  (regularity, interphase distance)

  * Composites
  Particle and fibre composites
  Immiscible liquids (monotectics)
  Foam materials

TECHNOLOGICAL INTEREST IN μ-G STUDIES ON SOLIDIFICATION OF CASTINGS

MACROSCOPIC SCALE

- MACROSEGREGATION

MICROSCOPIC SCALE

- MULTIPLICATION OF DENDRITES
- TRAPPING OR PUSHING OF INCLUSIONS
  (OXYSULFIDES - SILICA, ALUMINA)
- AGGLOMERATION OF INCLUSIONS
- MICROPOROSITY FORMATION
  (BY VOLUME SHRINKAGE OR EVOLUTION OF GAS
  DURING SOLIDIFICATION)
- HETEROGENEOUS NUCLEATION

ATOMIC SCALE

- MASS TRANSPORT AT THE LIQUID-SOLID INTERFACE

EXPERIMENTS IN MICRO - G:

- SEPARATION OF PURELY DIFFUSION CONTROLLED FROM CONVECTION CONTROLLED TERMS OF TRANSFER
- STUDY OF DENDRITE GROWTH
- CONSTITUTIONAL SUPERCOOLING
- FEEDING MECHANISMS (CONTROL OF VOLUME SHRINKAGE)

IMPORTANCE FOR EARTH PROCESSING:

- IMPROVEMENT OF PROPERTIES BY CONTROLLED SOLIDIFICATION OF INGOTS AND PRECISION CAST PARTS

DIRECTIONAL SOLIDIFICATION OF METALLIC ALLOYS

- MASS TRANSFER IN THE LIQUID BY DIFFUSION AND CONVECTION

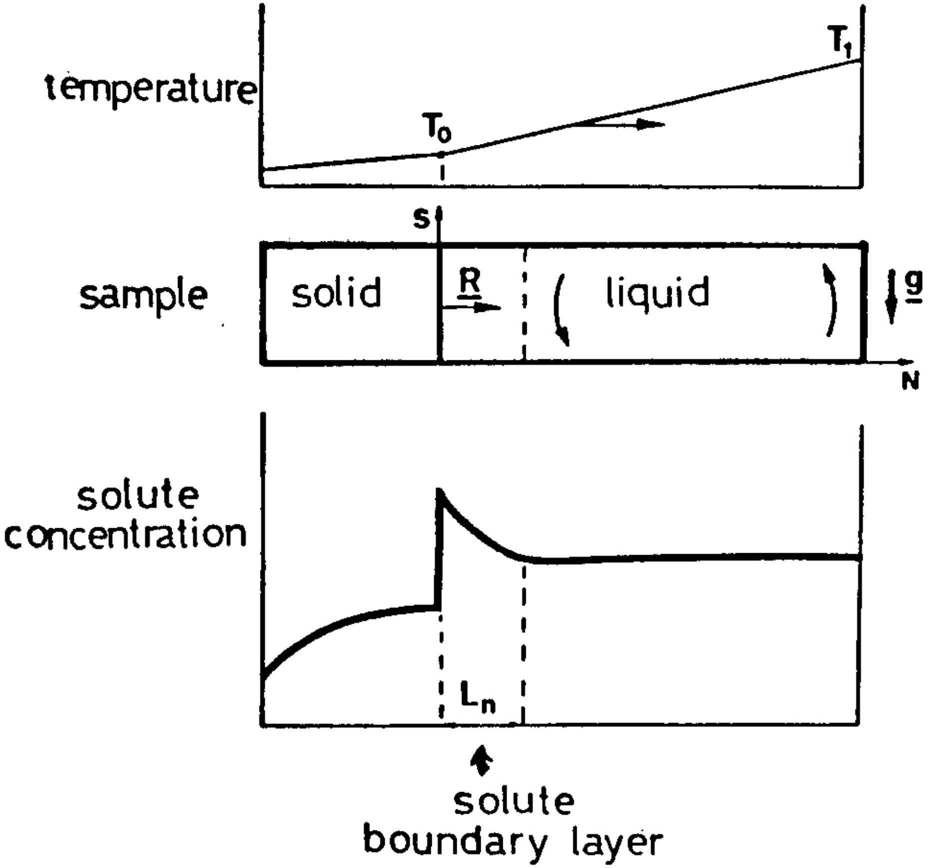
→ MACROSEGREGATION

- SOLUTE ENRICHMENT AT GROWING DENDRITES

→ MICROSEGREGATION

CONSEQUENCE: INHOMOGENEITIES OF ELEMENT DISTRIBUTION AND MICROSTRUCTURE LEAD TO INHOMOGENEOUS PHYSICAL PROPERTIES

(E.G. HIGH-STRESS PERFORMANCE
HIGH-TEMPERATURE MECHANICAL PROPERTIES
ACCELERATED CRACK GROWTH)



Bridgman solidification (schematic)

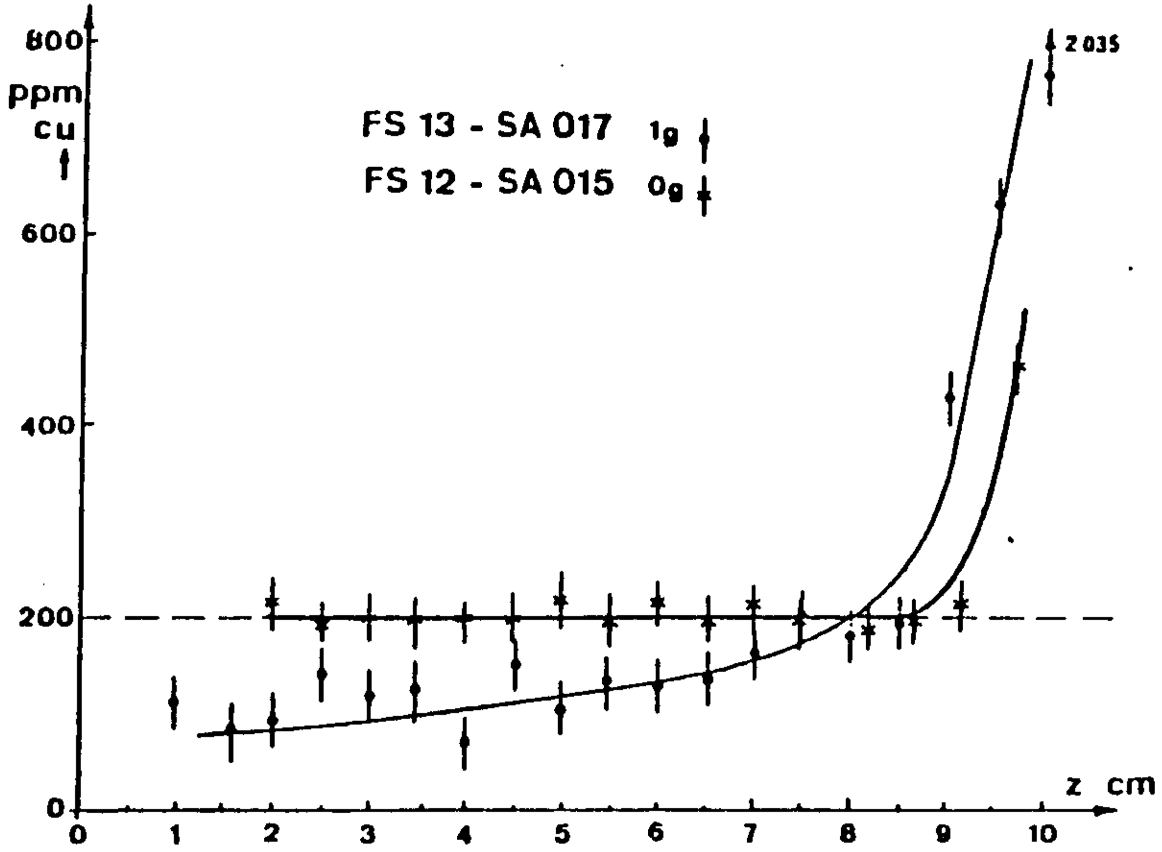
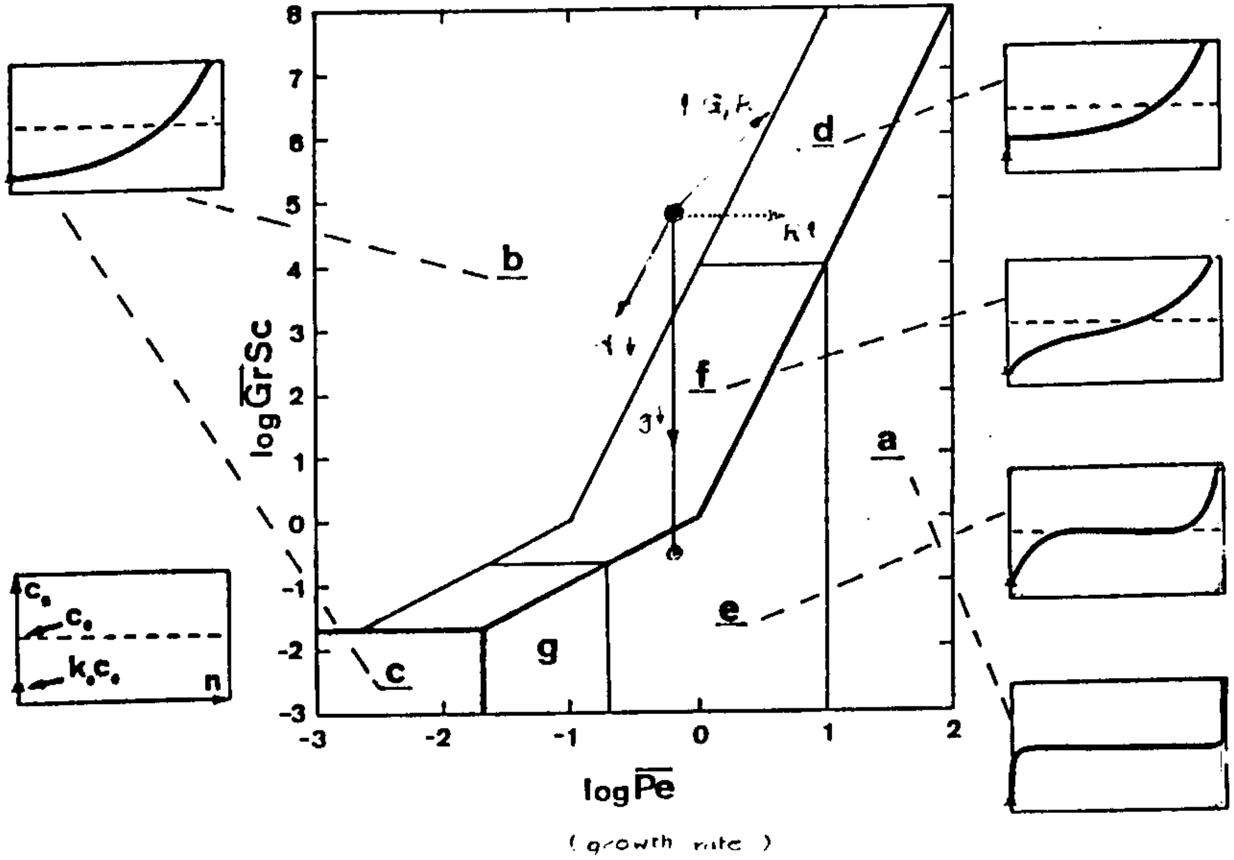
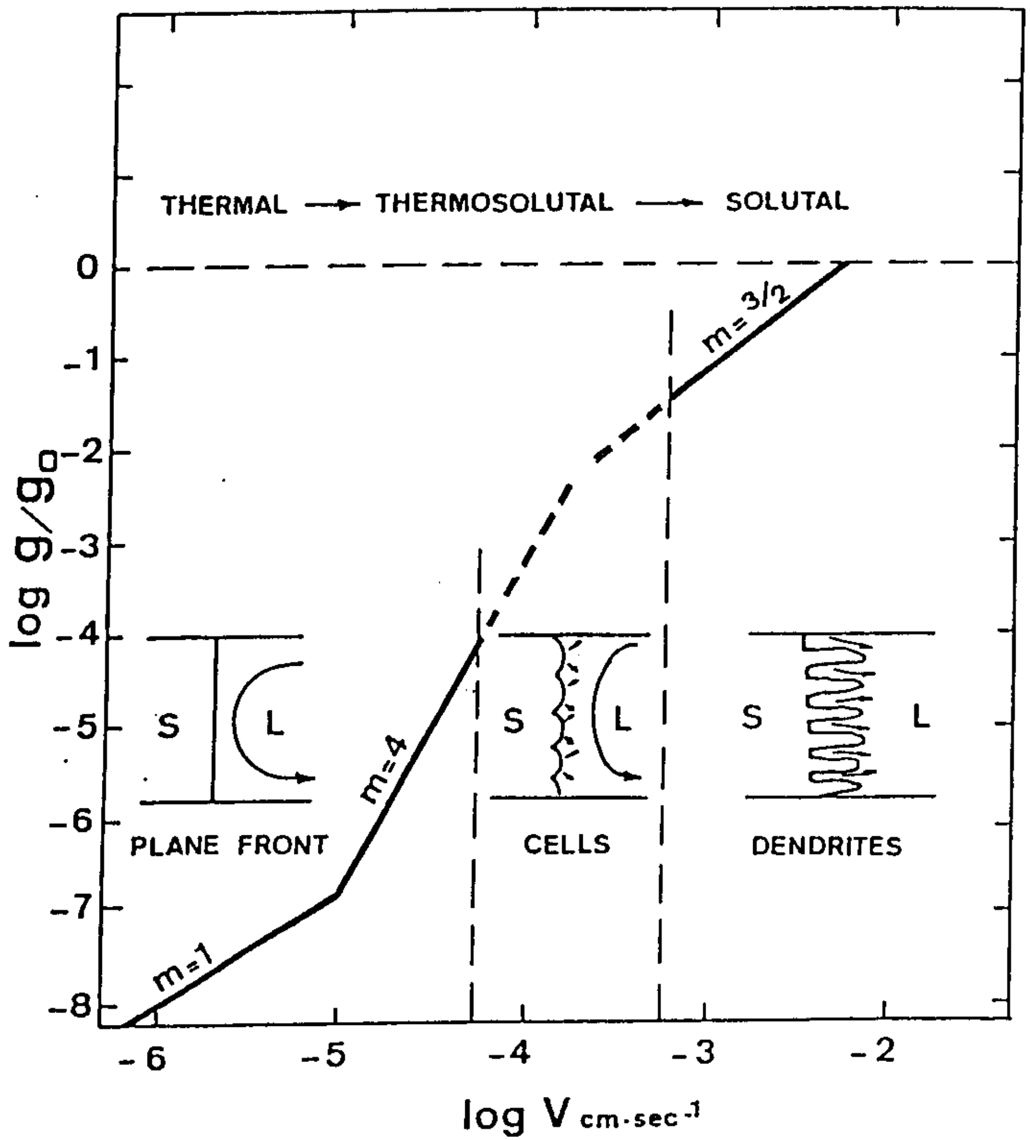


Fig. Longitudinal segregation profiles of copper in aluminium in the case of horizontal growth on earth (*FS* 13) exhibiting macrosegregation and in space (*FS* 12) showing an homogeneous concentration profile a part from the final transient


8
7
6
5
4
3
2
1
0
-1
-2
-3
log $\overline{Gr}$Sc
-3
-2
-1
0
1
2
log $\overline{Pe}$
(growth rate)
↑ G, R
R ↑
g ↓
a
b
c
d
e
f
g
c_s
c_0
k_0c_0
n



Al-Cu
$G = 25\ K.cm^{-1}$
$C = 20\%\ Cu$

Maximum allowed stationary g-level to get convection-free solidification in the range of solidification rates covering both planar and dendritic fronts.

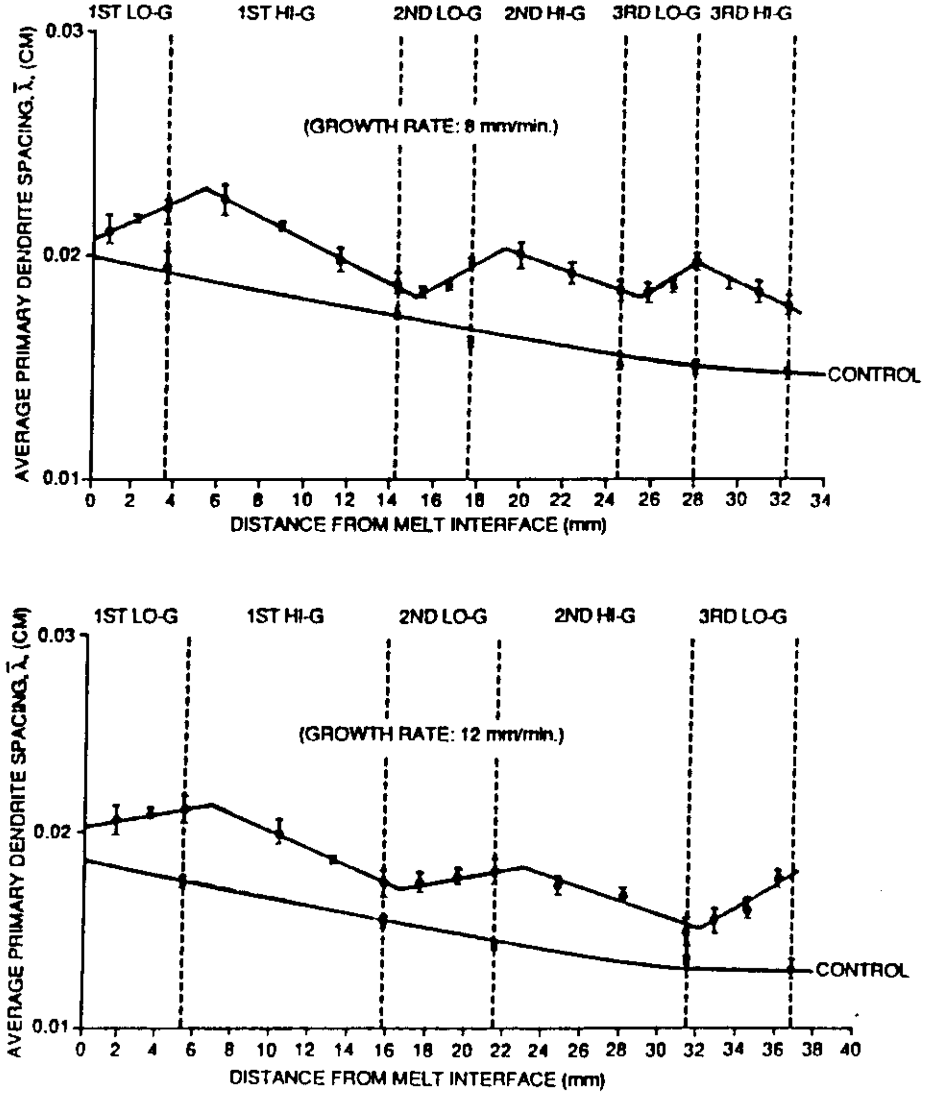


Fig. —Primary dendrite spacing for PWA-1480 superalloy directionally solidified during aircraft low-gravity parabolas. $G = 255$ °C/cm.

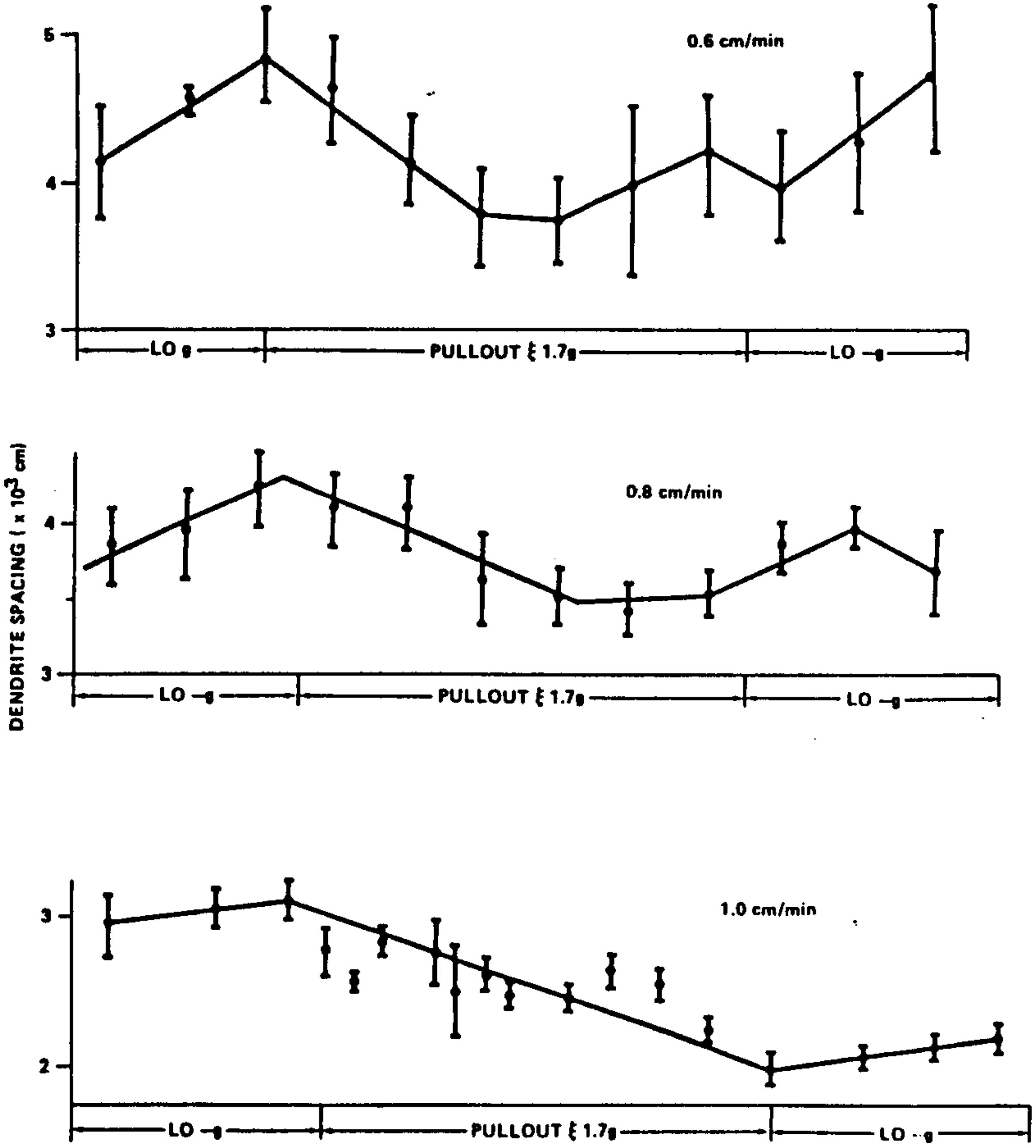
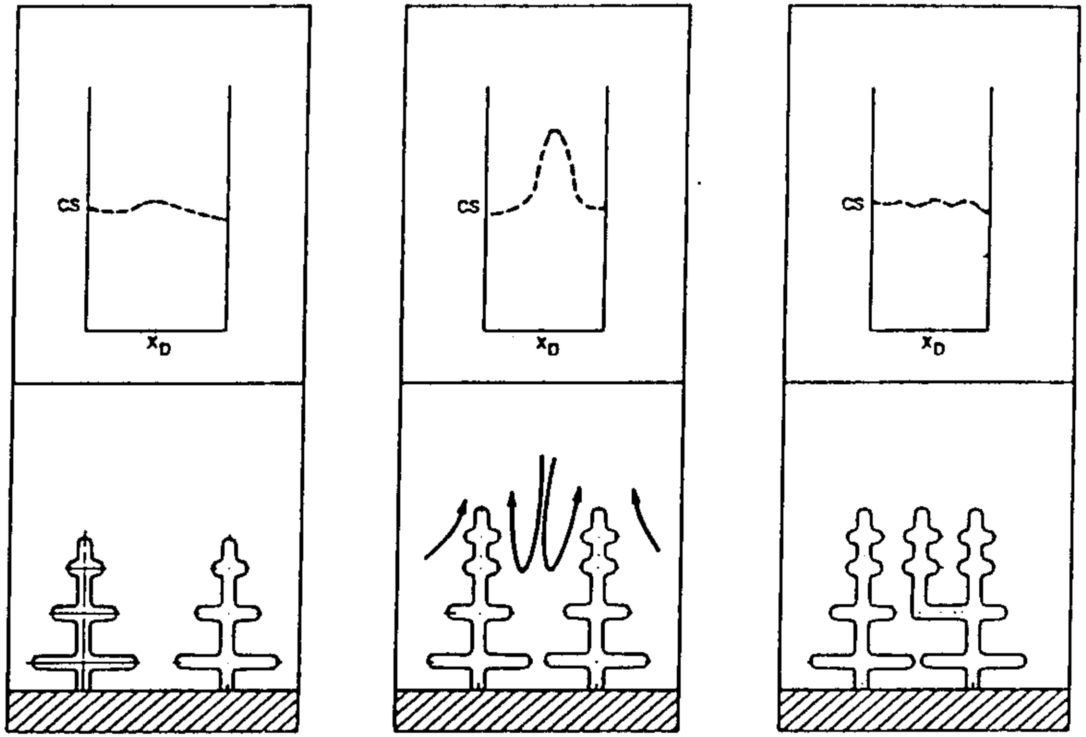


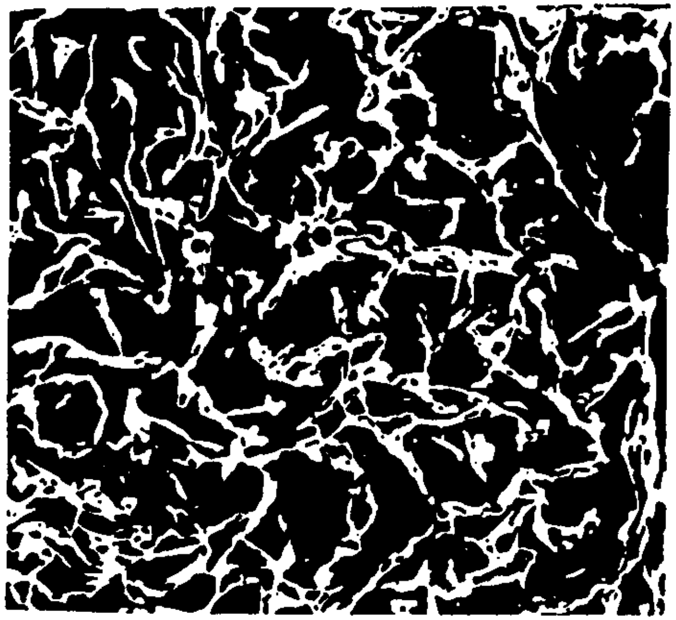
Fig. 1 — The variation of secondary dendrite arm spacings with gravity level in KC-135 sample at three solidification rates



(A) LOW - GRAVITY (B) HIGH - GRAVITY (C) HIGH - GRAVITY

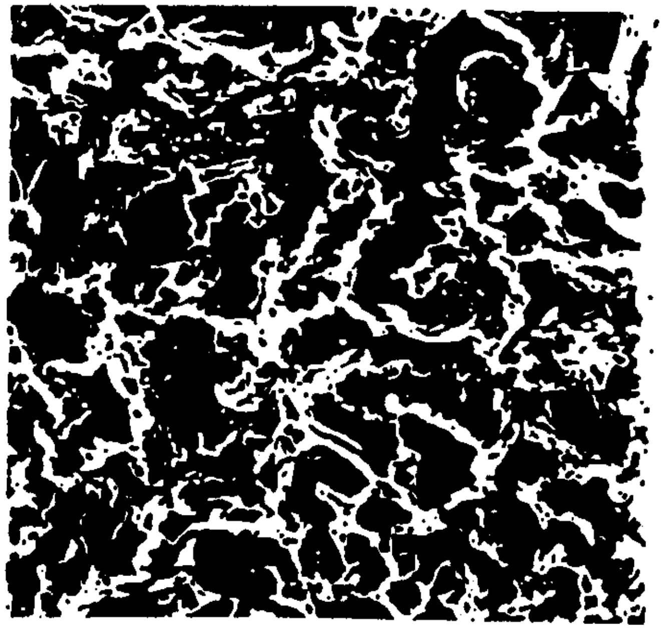
Fig. —Mechanism for decreasing primary dendrite spacing during directional solidification during low-gravity to high-gravity portion of aircraft parabolas. (*a*) Dendritic growth in low gravity. Solute transport is by diffusion. (*b*) Dendritic growth continues in high gravity. Solute transport is increased by buoyancy-driven convection. Interdendritic constitutional supercooling increases. (*c*) Ternary arm driven by increased constitutional supercooling grows to the dendrite tip growth front, decreasing interdendritic spacing.

Directional Solidification of Cast Iron



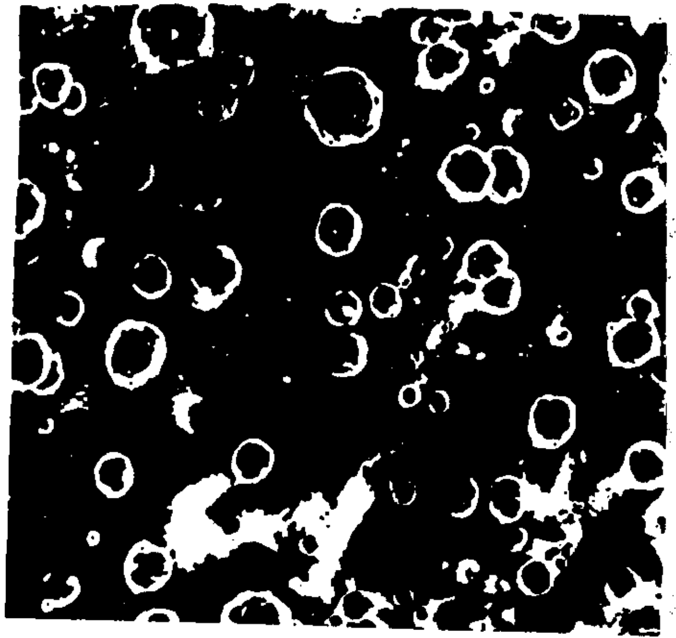
Grey Iron

brittle, due to
C flake edges



Compact Cast Iron

rounded edges



Ductile Iron

spheroidal graphite

increased strength and ductility

Goals of μ-g experiments on solidification of cast iron

1) John Deere and Co., Bethlehem Steel
   Univ. of Tuscaloosa

   PROCESS MANAGEMENT
   - CARBON FLOTATION
   - HIGH CARBON IRON PHASE DIAGRAM
   - CELL SIZE CONTROL
   - DIFFUSION MEASUREMENT LIQUID-SOLID
   - QUANTIFY DIFFERENCE CAUSED BY LACK OF CONVECTION

   DESIGN DATA
   - TRUE LIQUID THERMAL CONDUCTIVITY
   - PROPERTIES OF HIGH CARBON

   NEW MATERIALS

2) MAN Technologie SL 1, D 1
   Delft Inst. of Technology

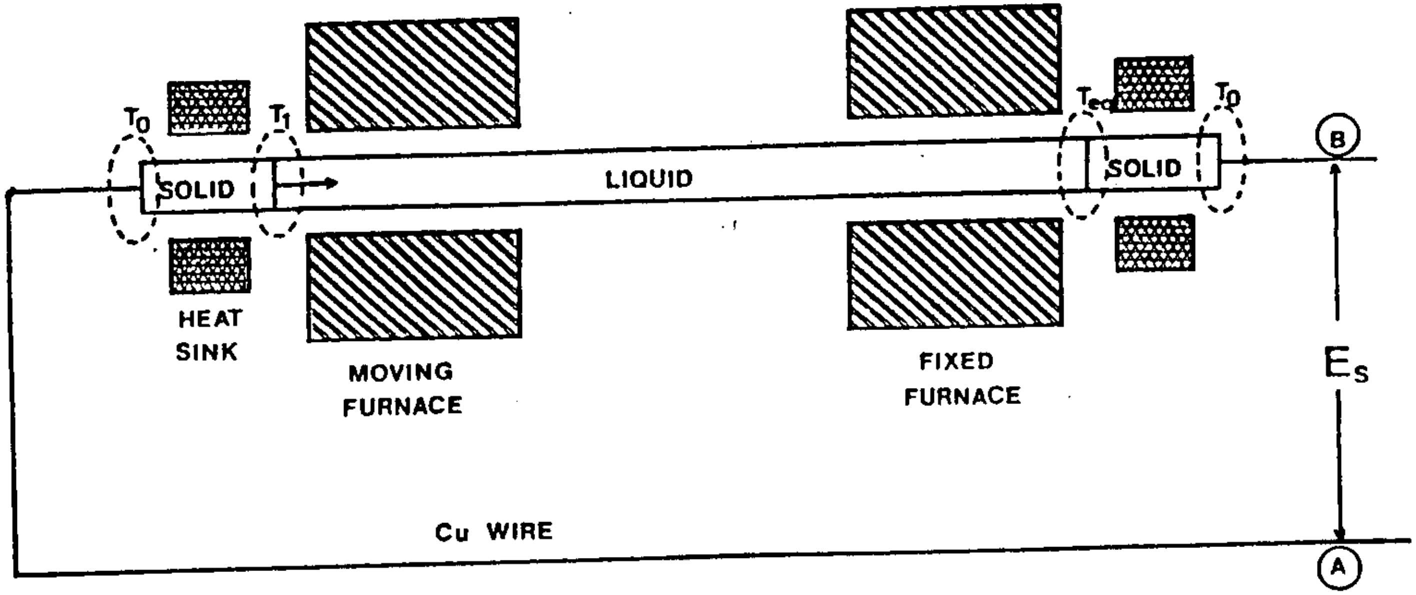
   - influence of S and P on graphite microstructure
   - diffusion of S in liquid iron

GRAPHITE VOLUME) GREY IRON SOLIDIFIED IN THE KC-135 AIRCRAFT. BAND OF LARGE FLAKES CORRESPONDS TO LOW-GRAVITY AND THE REMAINDER TO HIGH GRAVITY SOLIDIFICATION.

Photograph courtesy of Dr. Peter A. Curreri, Marshall Space Flight Center

INTOSPACE

MEPHISTO Project



Sketch of the apparatus for the in-situ Seebeck measurement of the solid-liquid interface temperature during solidification

COMPOSITES

Regular arrangement of second phase inclusions

- solid particles, short fibres
- droplets
- gas bubbles

in a metallic matrix

Two different methods of preparation:

- In-situ generation of reinforcing phase
  - * eutectic alloys ($L \rightarrow \alpha + \beta$)
  - * monotectic alloys ($L \rightarrow L_1 + L_2$)
  - * precipitation of gas bubbles caused by
    - different solubility (e.g. H_2 in Al)
    - chemical reaction (e.g. $C + SiO_2 \rightarrow CO + Si$)

- Artificial preparation
  * melting and solidification of P/M alloys (dry mixing)
  * insertion of particles into the melt (wet mixing)

Problems: suppression of demixing in the melt reaction with the advancing melting or solidification front

DIRECTIONAL SOLIDIFICATION OF EUTECTIC ALLOYS

- THERMAL AND SOLUTAL CONVECTION GIVE RISE TO FAULTS AND TERMINATIONS DURING THE CONTROLLED GROWTH OF IN-SITU COMPOSITES

- CRITICAL G/V MUST BE MAINTAINED TO GET PLANAR GROWTH FRONT

- IN MULTIVARIANT EUTECTIC ALLOYS (OF TECHNICAL INTEREST) SEGREGATION EFFECTS LEAD TO INHOMOGENEOUS DISTRIBUTION OF ELEMENTS IN THE MELT AND TO GROWTH RATE FLUCTUATIONS. BOUNDARY LAYER OF THE ORDER D/V → LONG RANGE DIFFUSIVE TRANSPORT REQUIRED
  (PURE BINARY EUTECTICS: B.L. IN THE ORDER OF LAMELLAR SPACING)

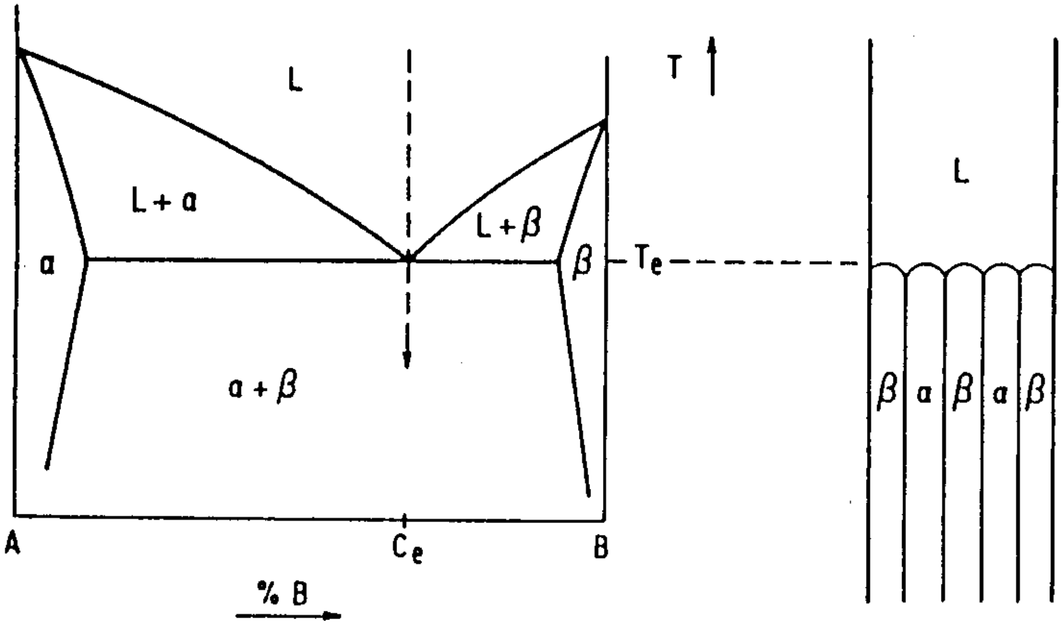


Fig. Phase diagram with directionally solidified eutectic. Phases α and β may be terminal phases or intermetallic compounds.

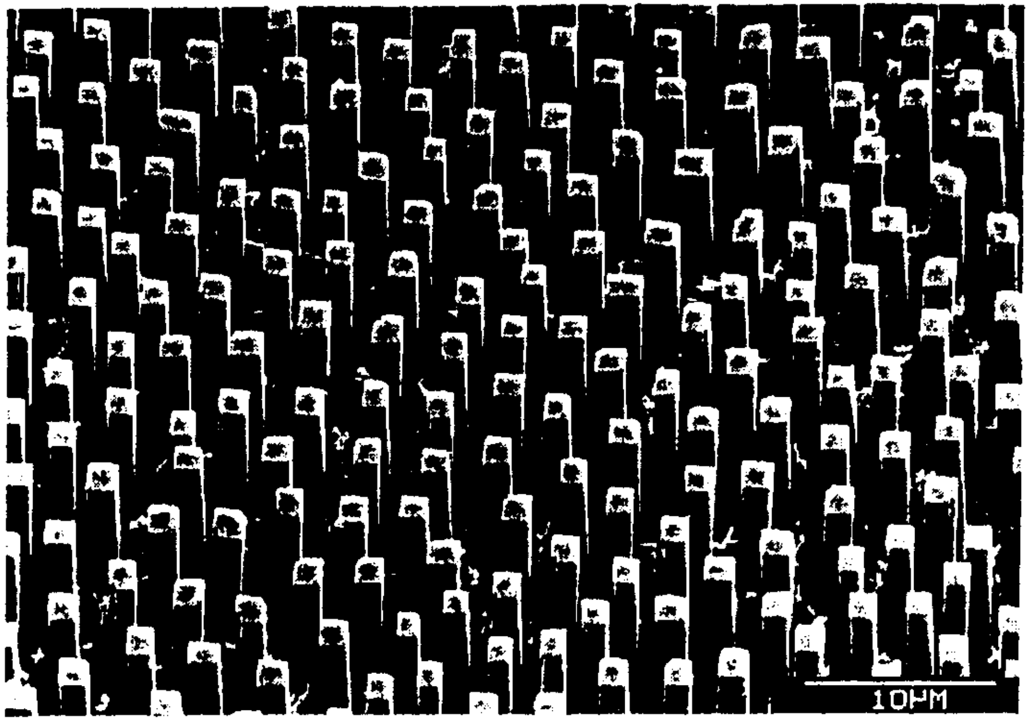


Fig. Transverse section of a directionally solidified monovariant eutectic alloy γ/γ'-α (Ni/Ni_3Al - Mo). The reinforcing molybdenum fibres have been isolated by selective etching.

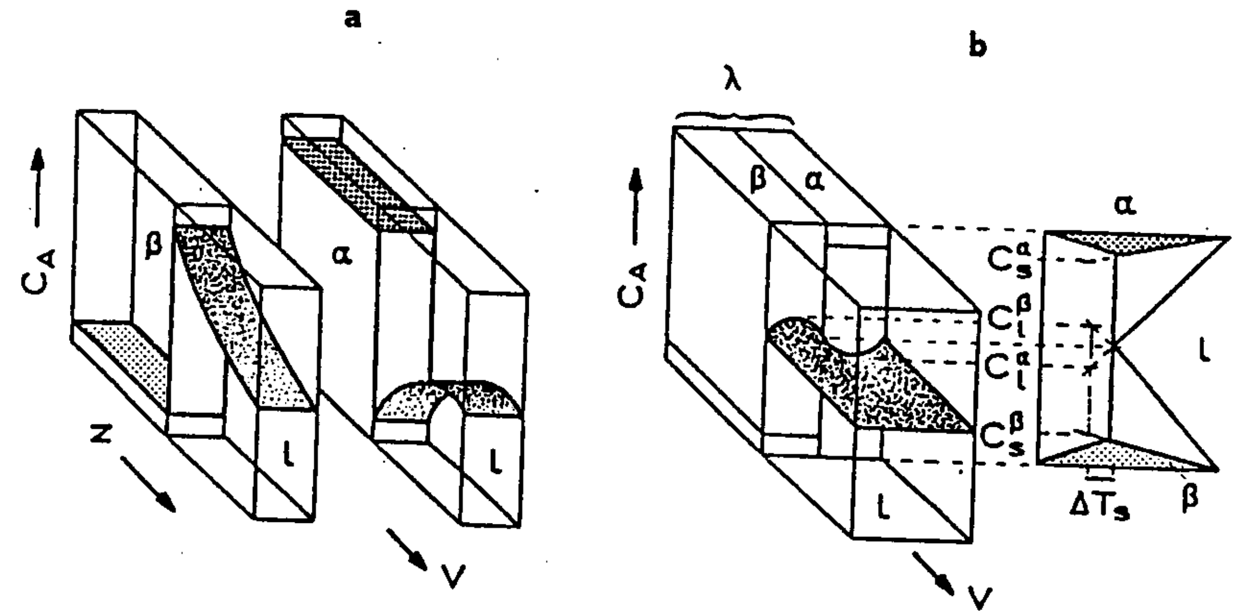
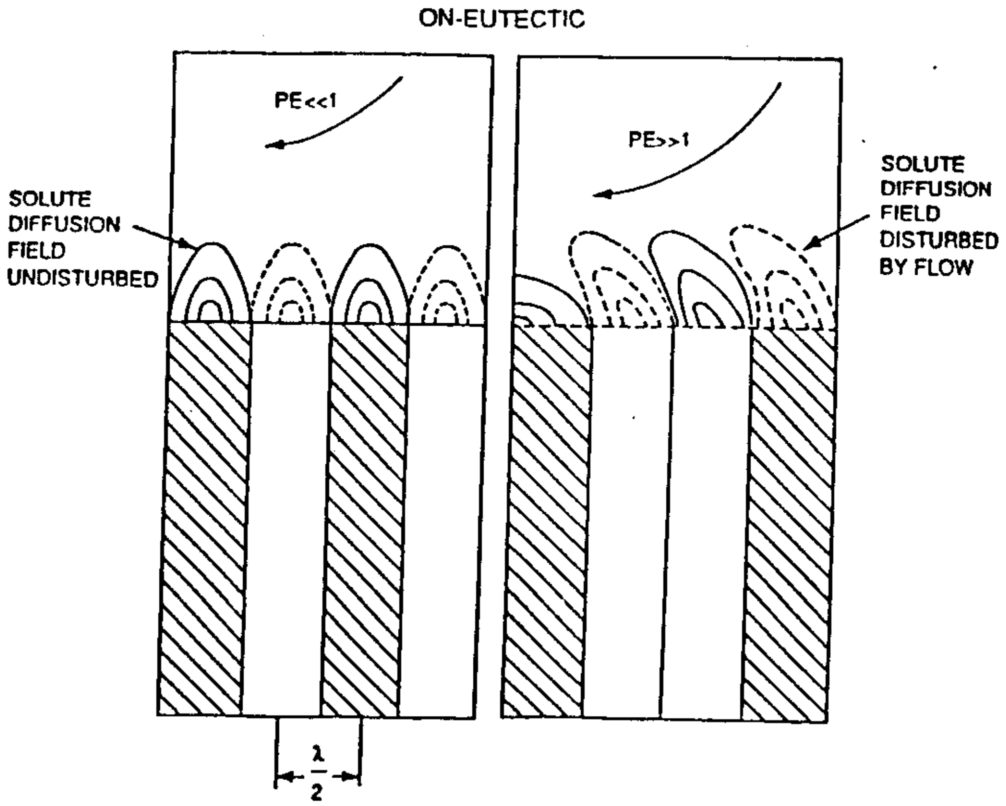


Figure :;EUTECTIC DIFFUSION FIELD

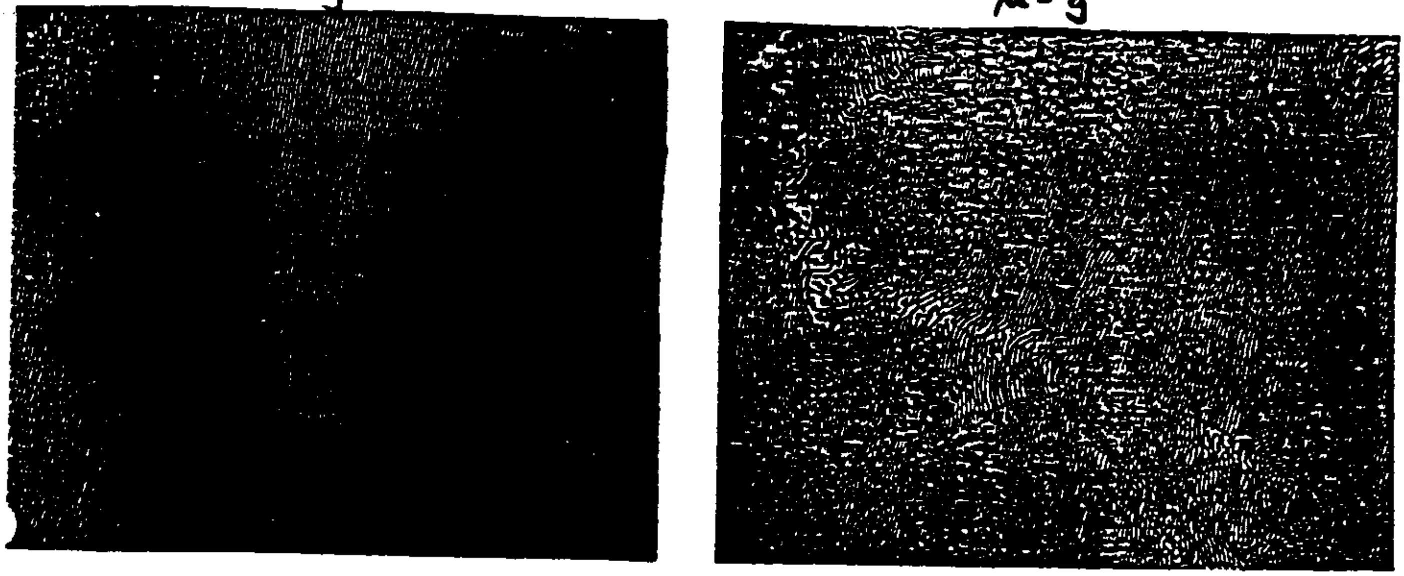


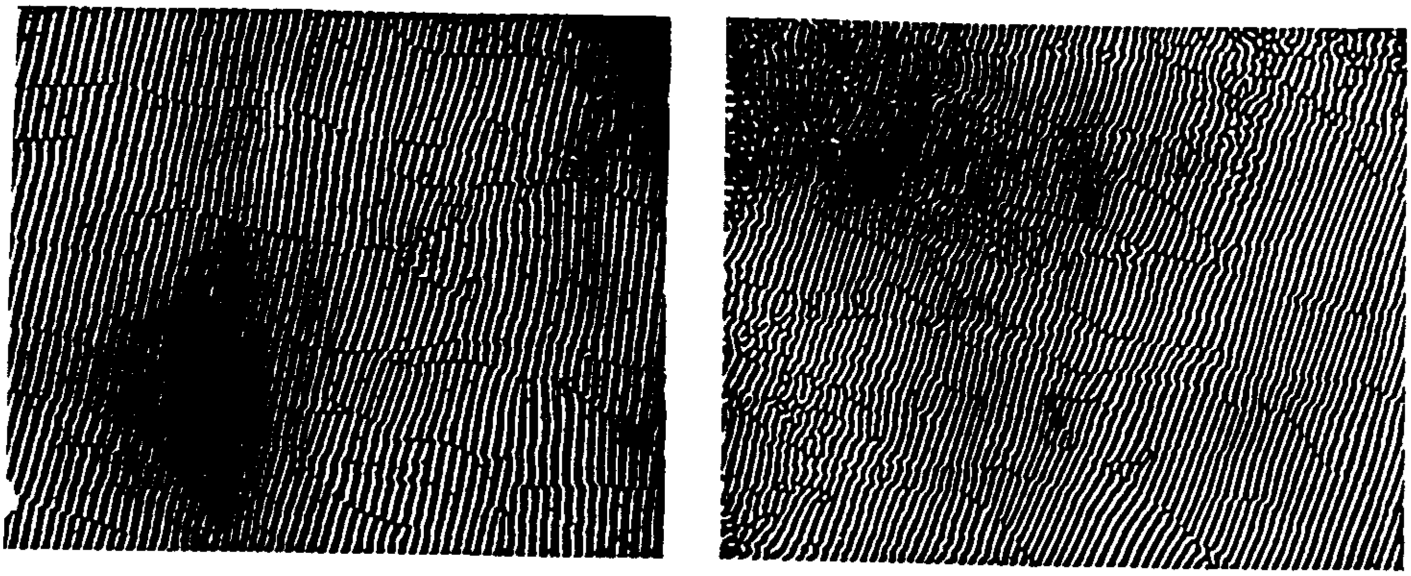
Schematic isoconcentration curves ahead of the growth interface for on-eutectic showing diffusion fields disturbed for high Pe and undisturbed for small Pe

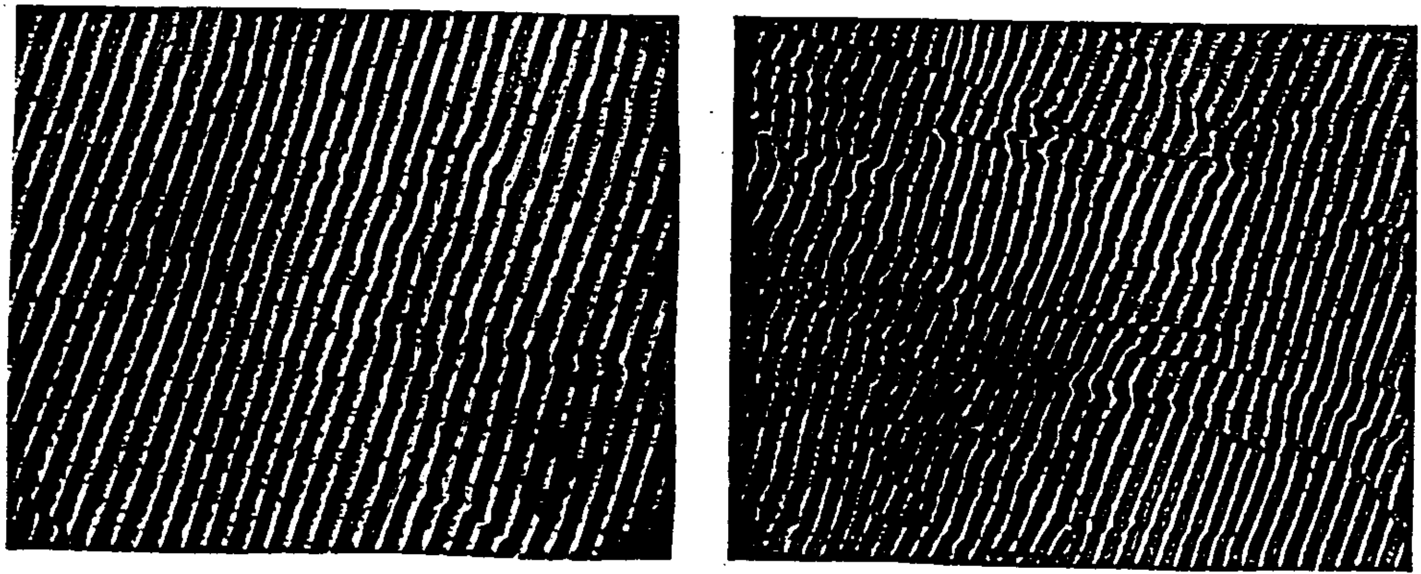
Structure transversale de l'eutectique
Al_2Cu-Al

Solidifié au sol
$Z = 27,9$ mm
$V = 5,2$ cm/h
1g

Solidifié en microgravité
$Z = 27,9$ mm
$V = 7,1$ cm/h
µ-g


X 200

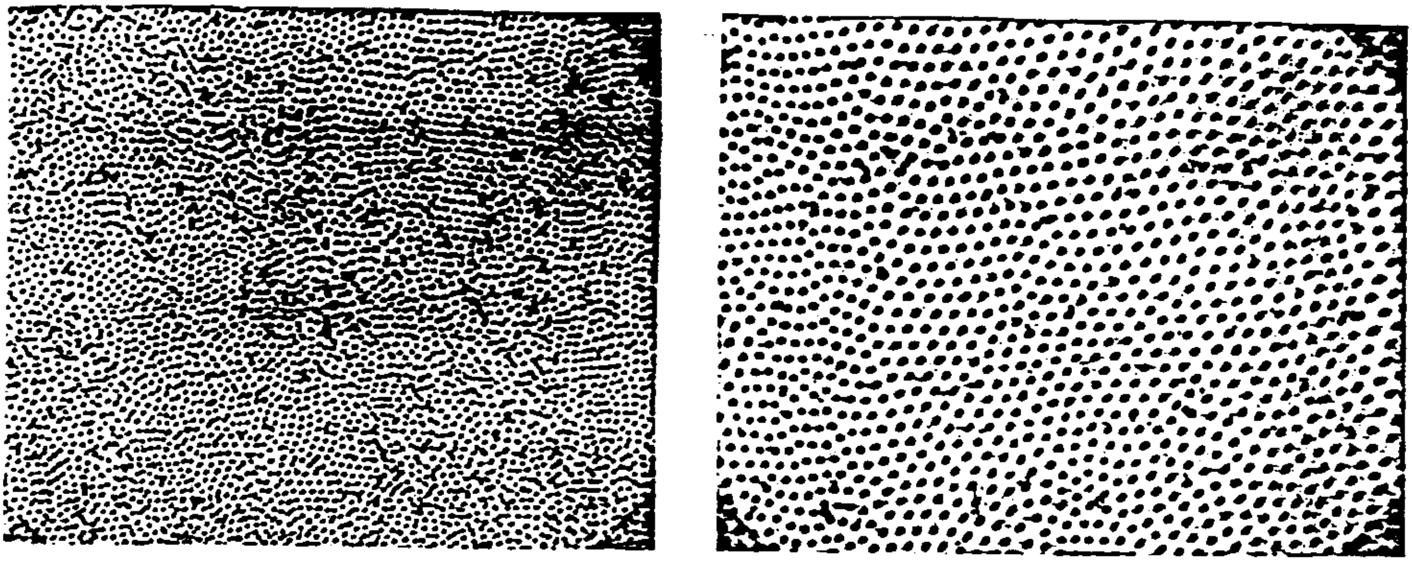

X 500


X 1000

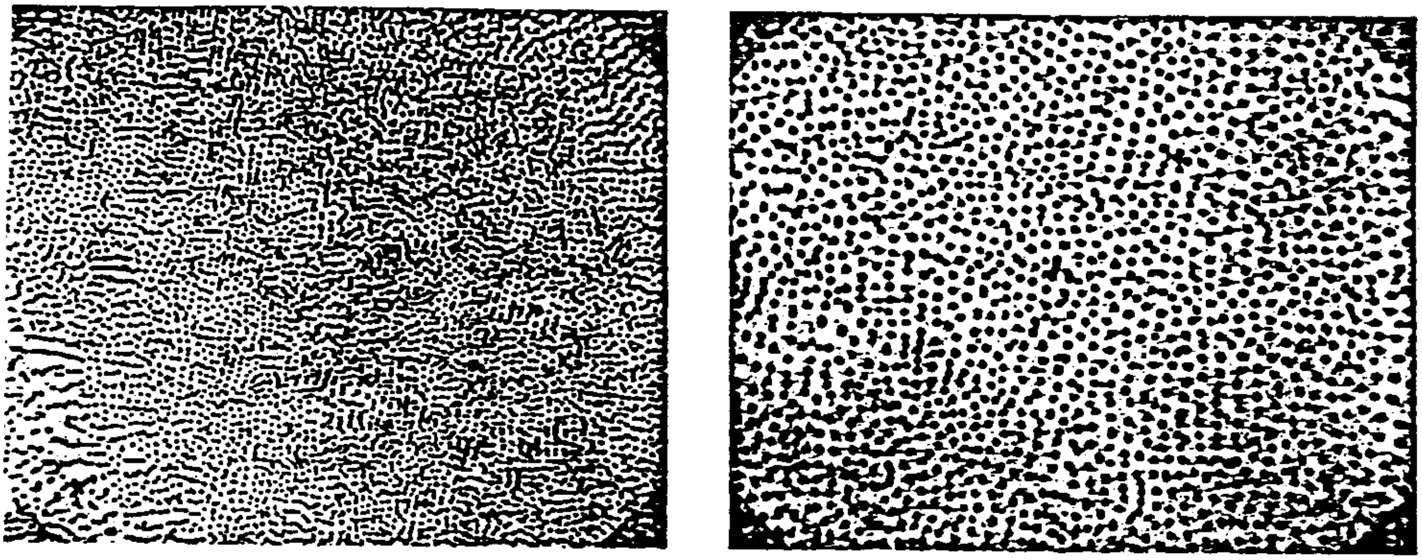
(Favier)

transversale de l'eutectique $\underline{Al_3Ni-Al}$
solidifié en microgravité

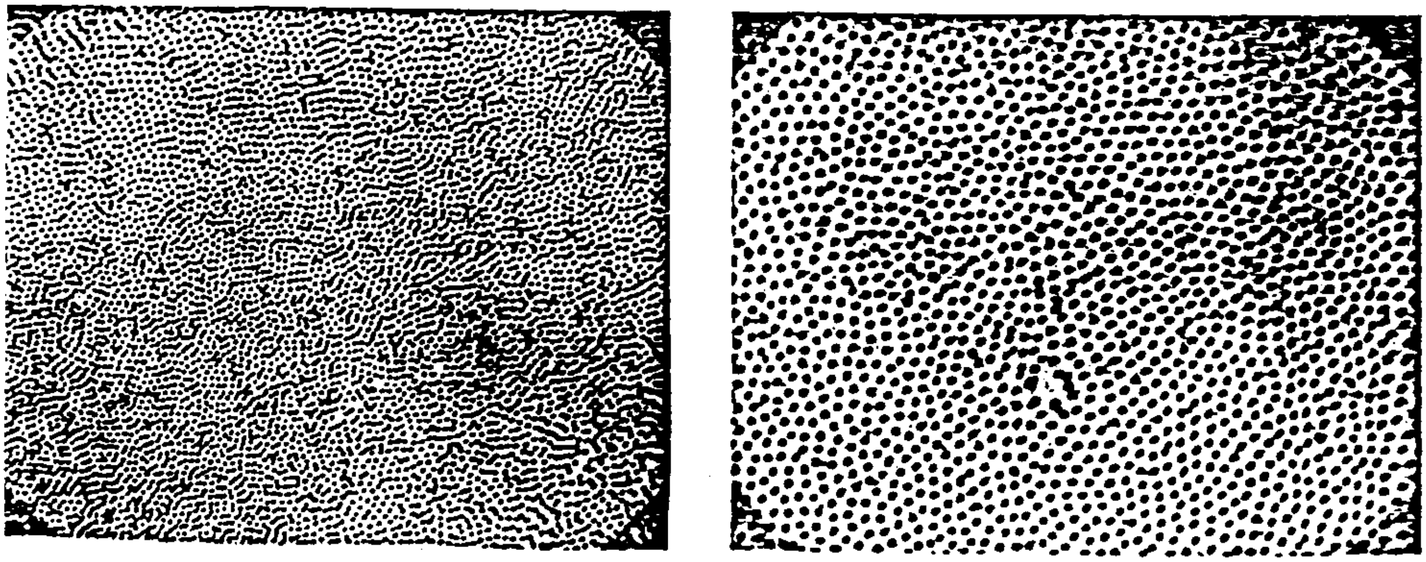
X 500 (m-g) X 1000



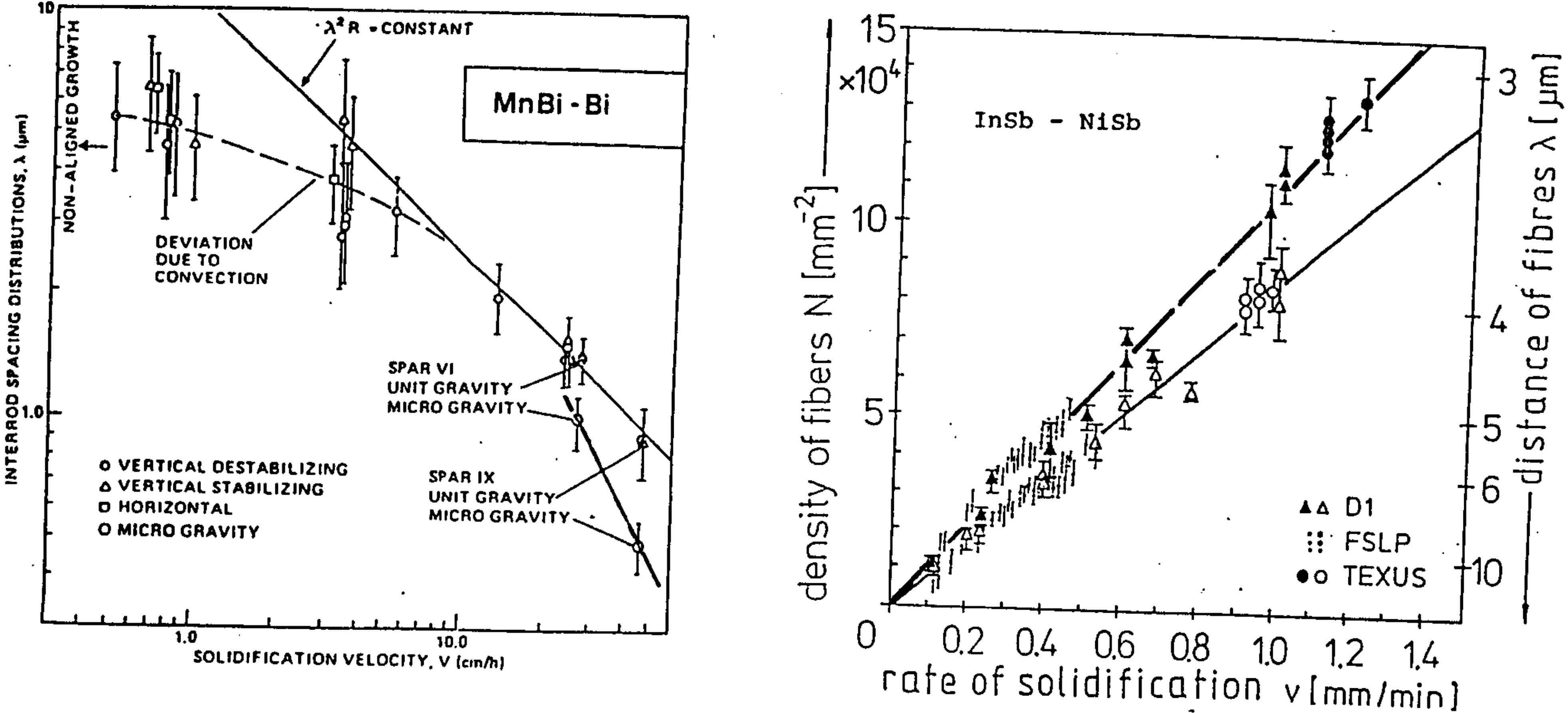
Z = 20,5



Z = 30,6



Z = 33,8



(Larson)

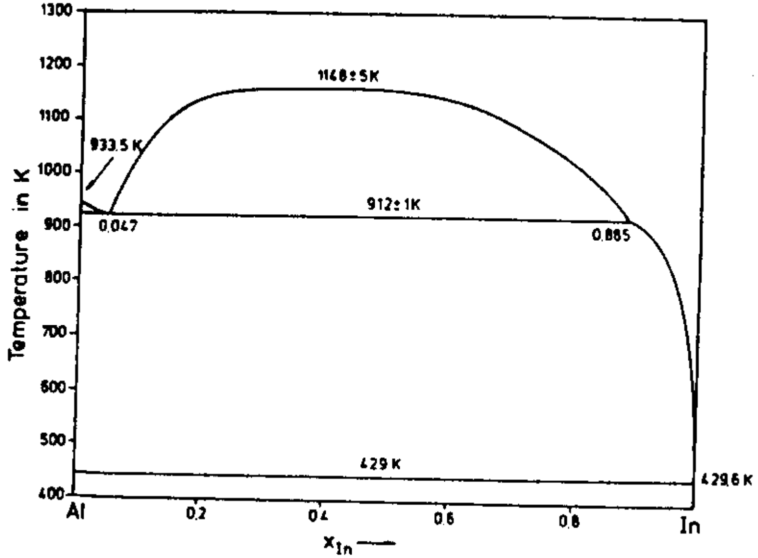
(Müller and Kyr)

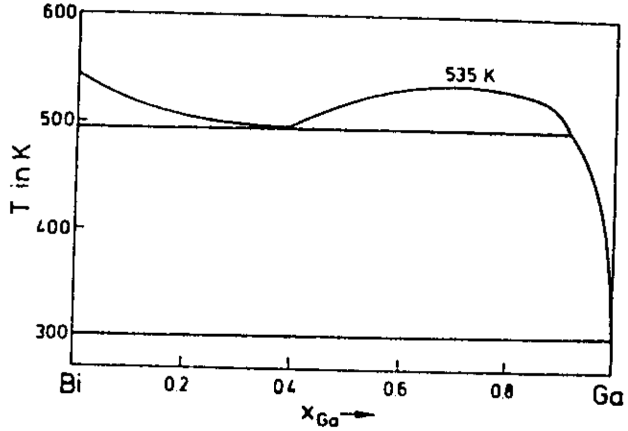
Influence of gravitation on interfibre distance
in eutectic alloys

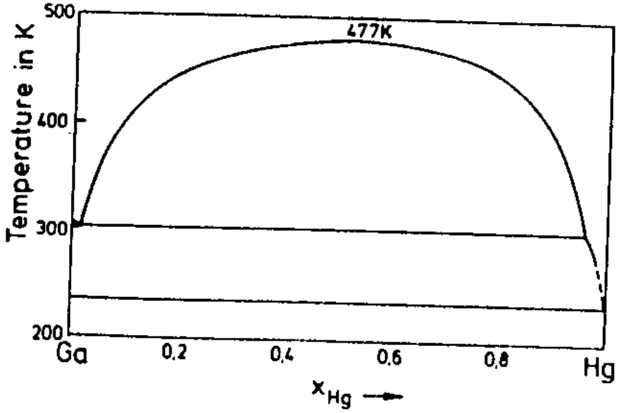
Effect of Low Gravity on On-Eutectic Interphase Spacing
(Various Authors)

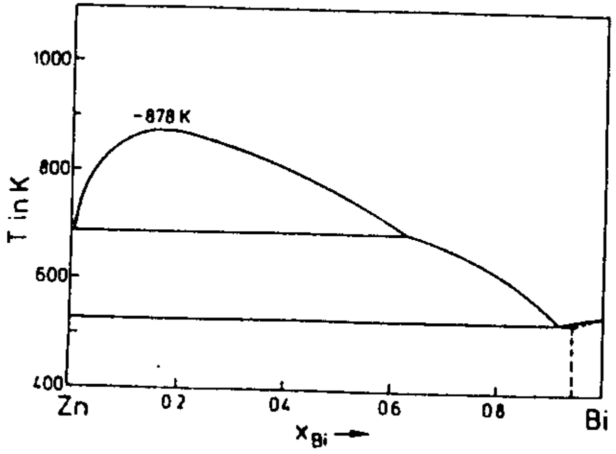
Alloy Composition	Low-Gravity Solidification Effect on Interphase Spacing
Lamellar Eutectics	
Al_2Cu/Al	no change
Fe_3C/Fe	- 25 %
Fibrous Eutectics	
MnBi/Bi	- 50 %
InSb/NiSb	- 20 %
Al_3Ni/Al	+ 17 %

Various Types of Miscibility Gap Phase Diagrams



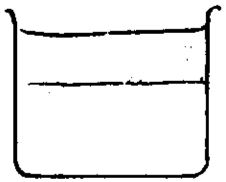




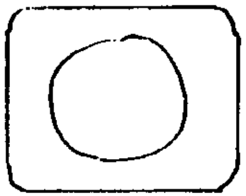


μ-g solidification of immiscible / monotectic alloys

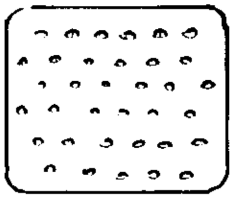
Goals : finely dispersed microstructure of two-phase alloys



1g



μ-g typical result



μ-g expected

knowledge of driving forces leading to agglomeration and separation
(wettability , Marangoni migration etc.)

→ prevention of reaching the equilibrium state

Joint project : "Monotectic alloys"

Industrial applications : bearing materials
Superconductors

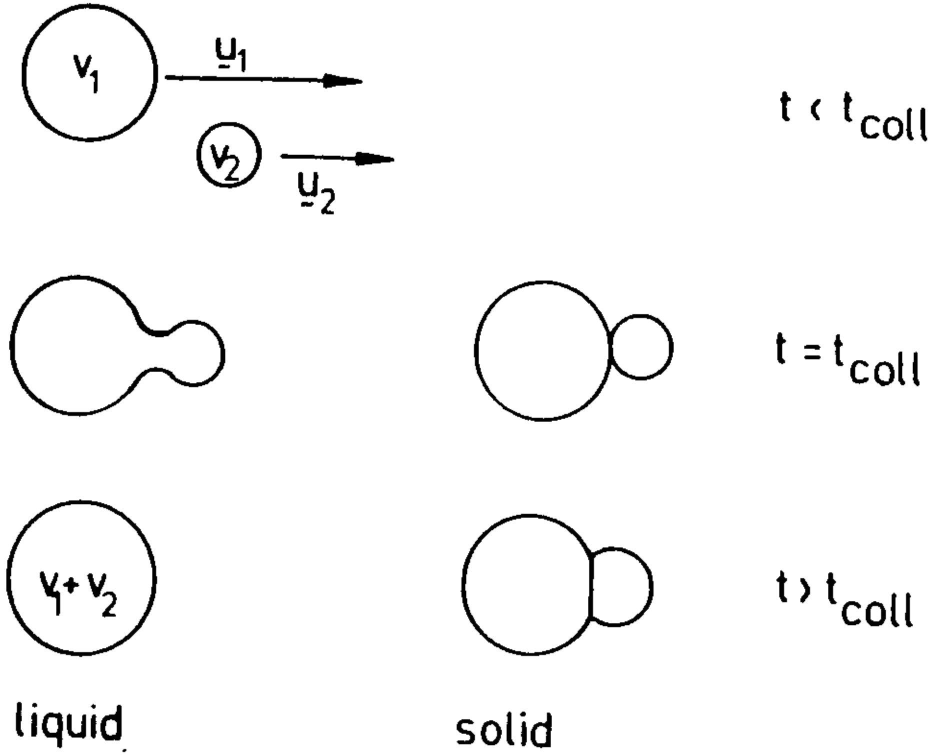


Fig. Schematic diagram showing the way a collision of droplets with subsequent coagulation may occur

$$\text{Liquid 1} \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftarrows}} \text{Solid } \alpha + \text{Liquid 2} \xrightarrow[\text{further cooling}]{} \text{Solid } \beta$$

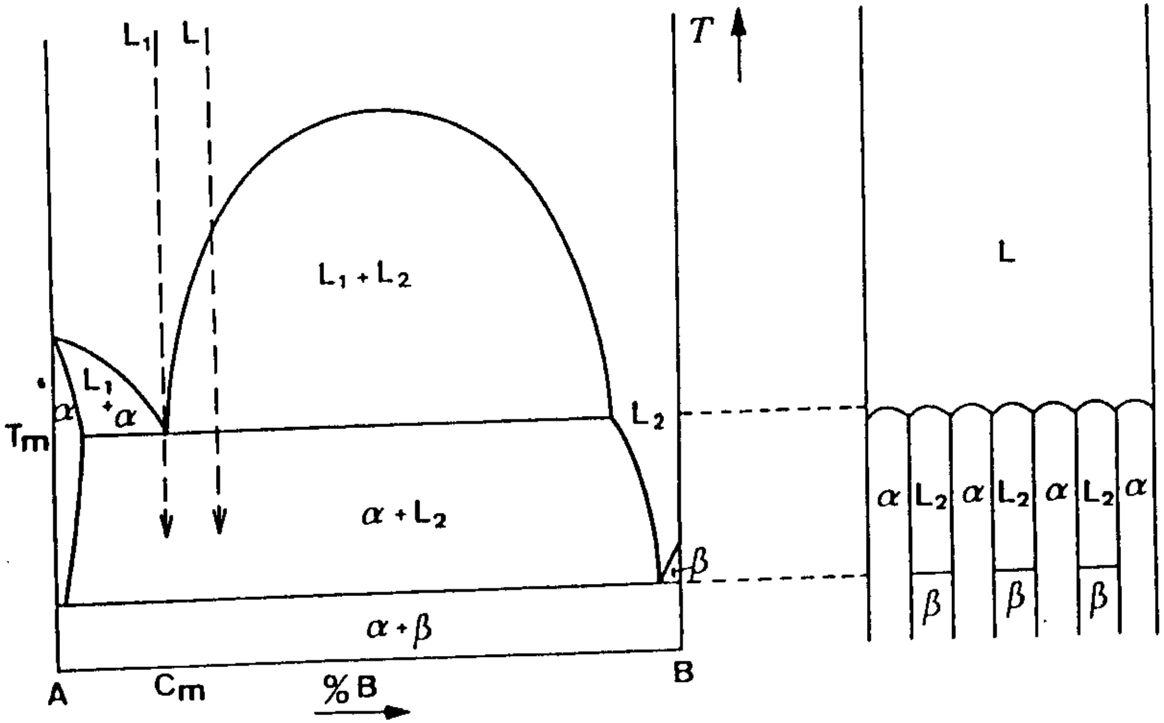


Fig.5 (a) Phase diagram with monotectic. (b) Directional solidification of liquid L_1 of composition C_M may produce an aligned structure of α and β phases.

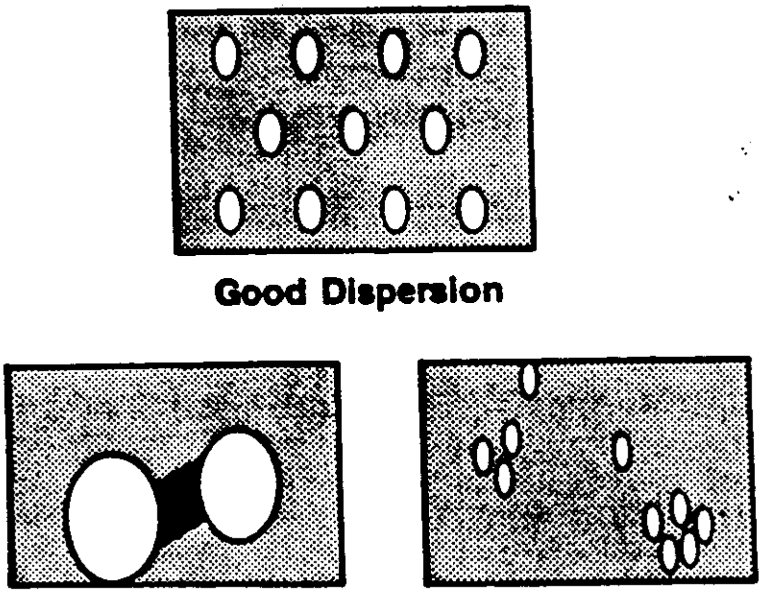
SOLIDIFICATION OF PARTICLE COMPOSITES

- GRAVITY SEGREGATION (STOKES)

  $v_s = d^2 \cdot g \cdot (\rho_m - \rho_p) / 18\eta$

- AGGLOMERATION OF PARTICLES BY
  - CONVECTION INDUCED MOTION
  - BROWNIAN MOTION

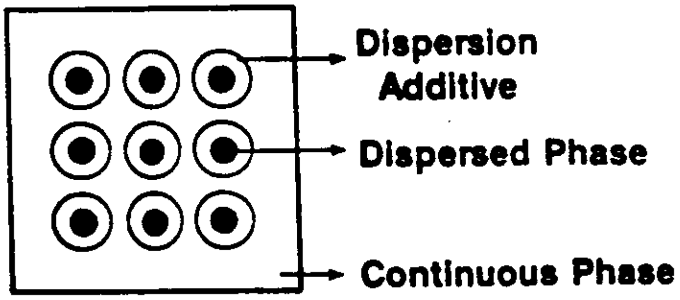
- PUSHING OF PARTICLES BY THE ADVANCING SOLIDIFICATION FRONT



Good Dispersion

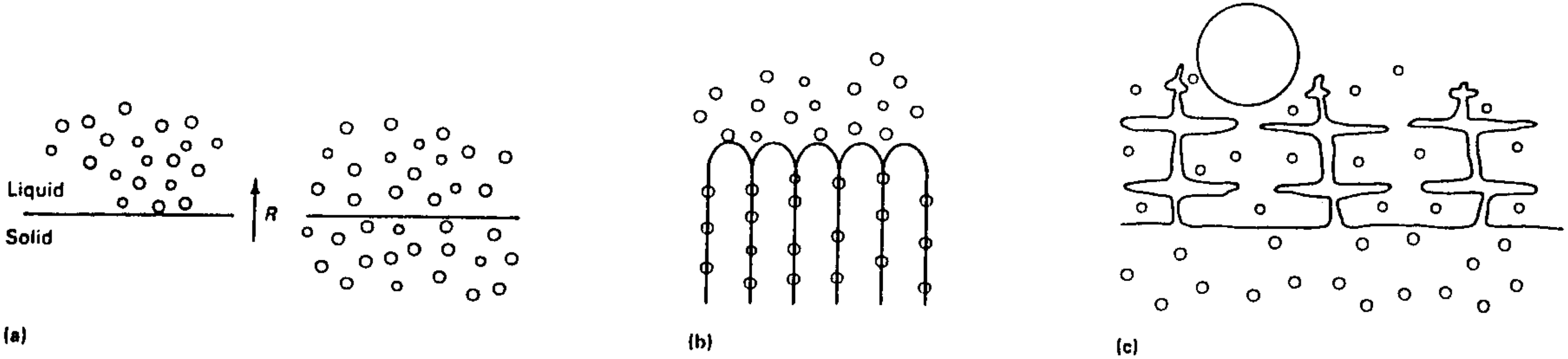
Poor Dispersions

FIGURE COMMERCIAL PHASE DISPERSIONS

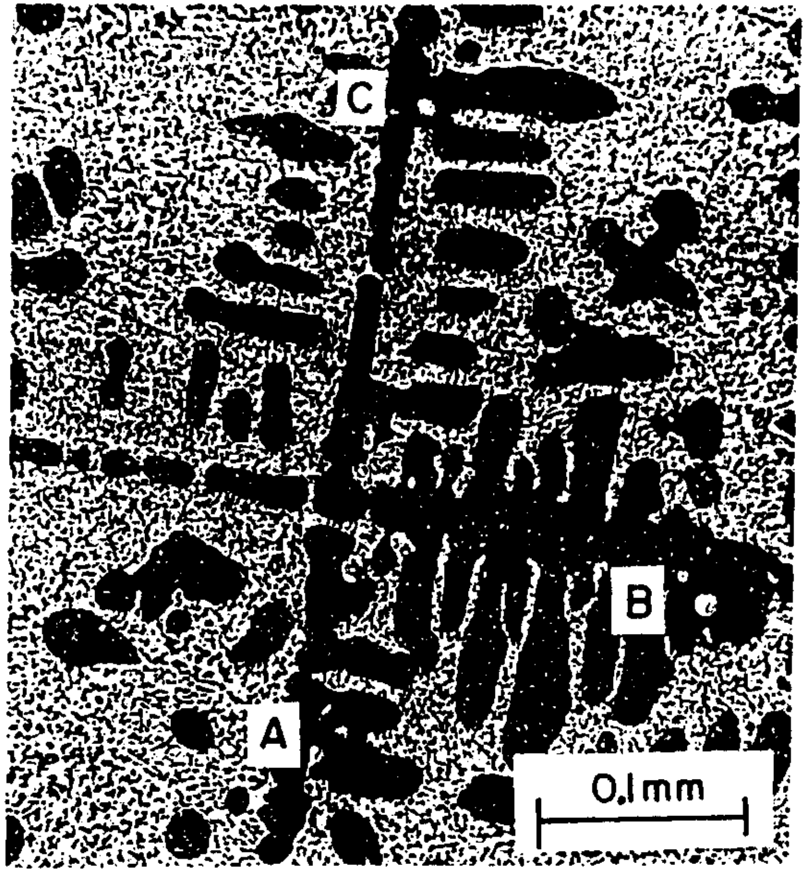


Response = f (Density, Surface Tension, Viscosity, Particle Size/Distribution, Temperature, Gravity, Cure Kinetics, Mixing Rate, Additives)

FIGURE . OPPORTUNITIES FOR DISPERSION TECHNOLOGIES



Influence of interface shape on pushing or entrapment of particles. (a) Planar interface can result in pushing (left) or engulfment (right). (b) Cellular interface showing pushing at interface and entrapment between cells. (c) Dendritic interface; small particles are entrapped in interdendritic spaces while large particles are pushed.



Iron particles entrapped in interdendritic regions in a cast Pb-50Sn alloy

Relevant experimental results of low-gravity experiments on composite materials

Pötschke (Krupp Fl)

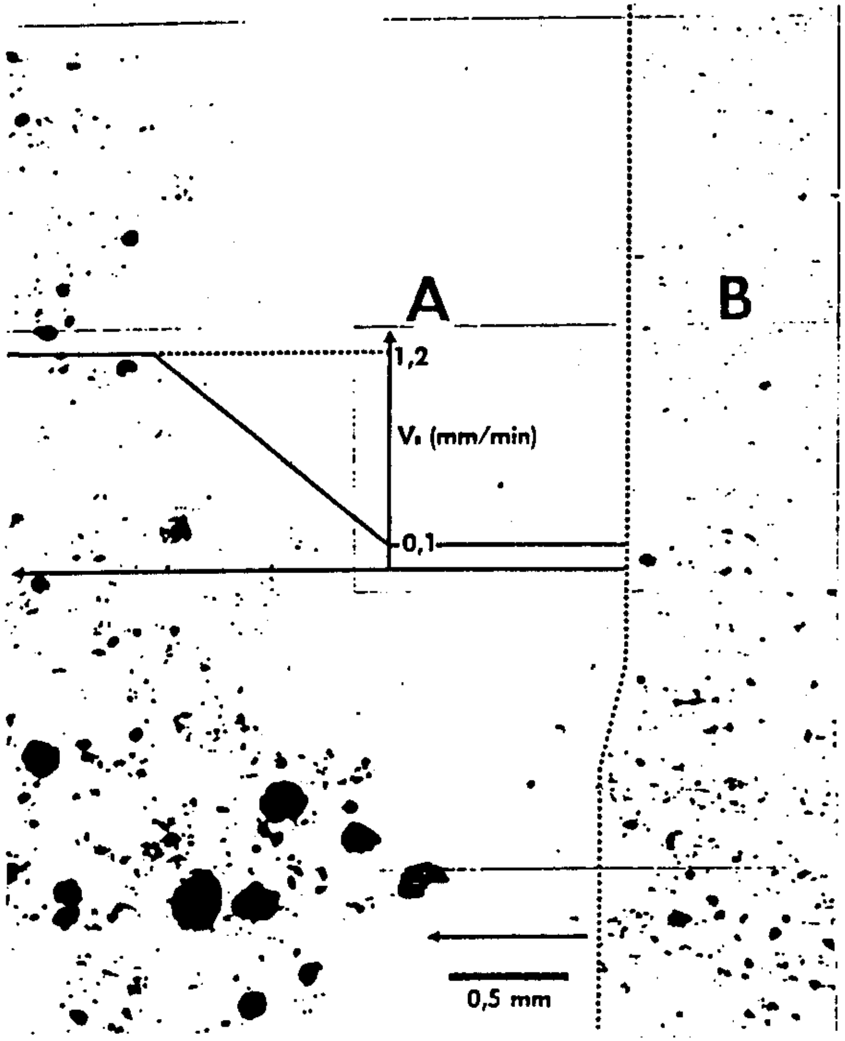
- Critical growth rate for engulfment of particles

Froyen, Deruytterre (KU Leuven)

- Agglomeration of particles with respect to wettability

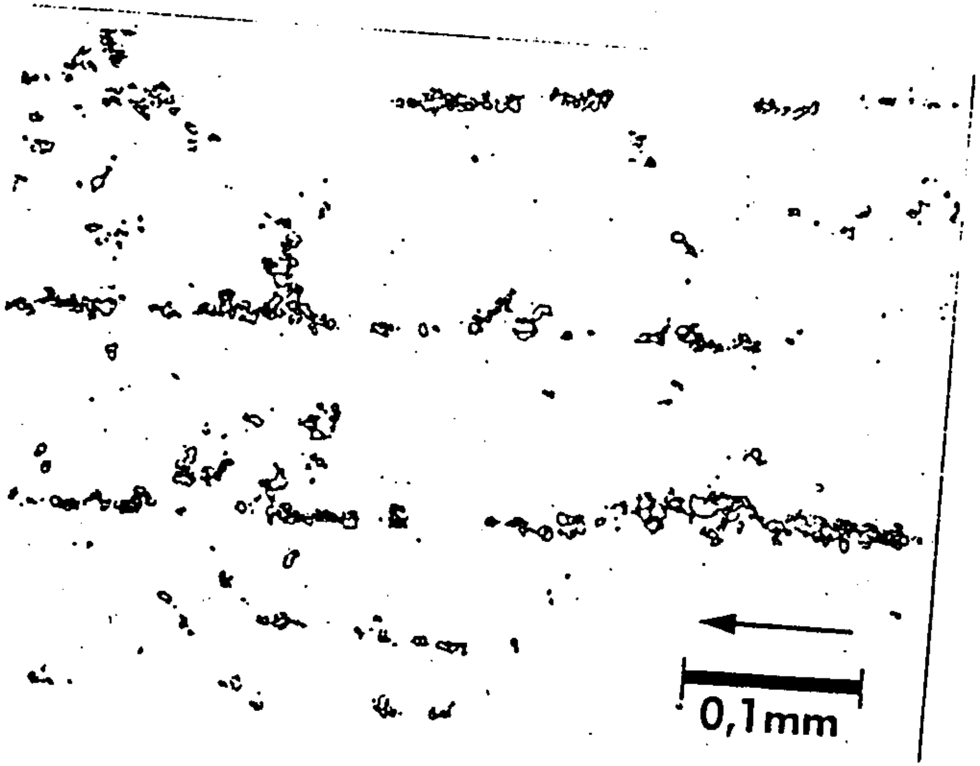
Frederickson (RIT Stockholm)

- Critical volume content of solid or liquid particles for avoidance of agglomeration

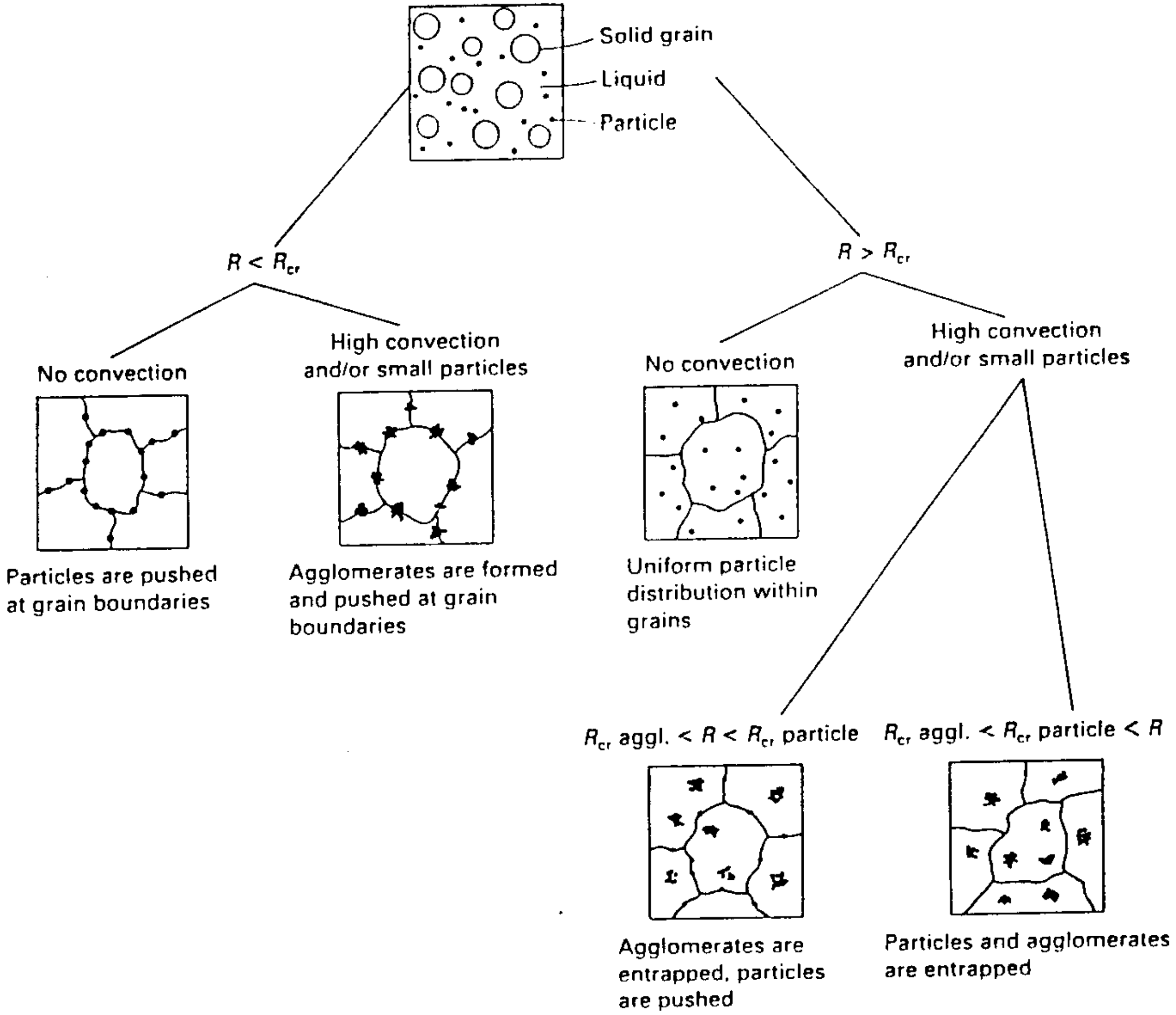


Rejection and engulfment of Al_2O_3 particles in a copper melt by the advancing growth front

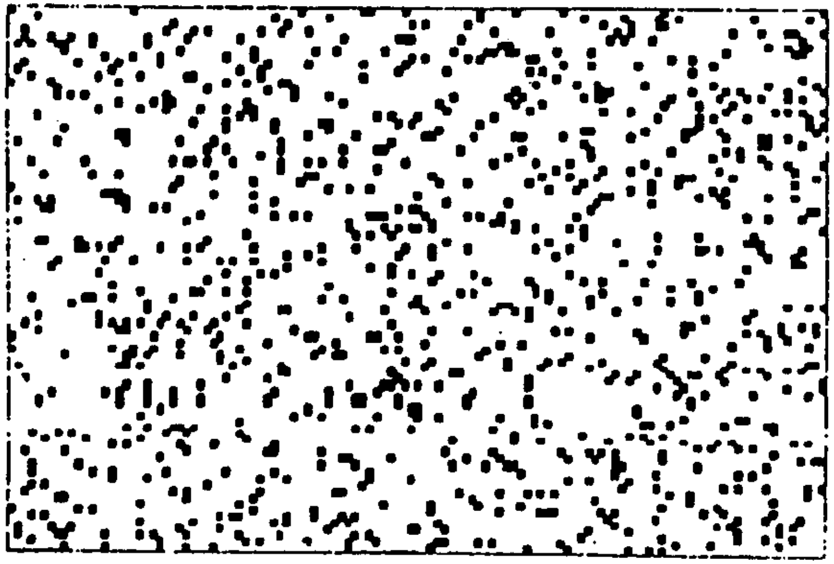
(after Pötschke, D-1)

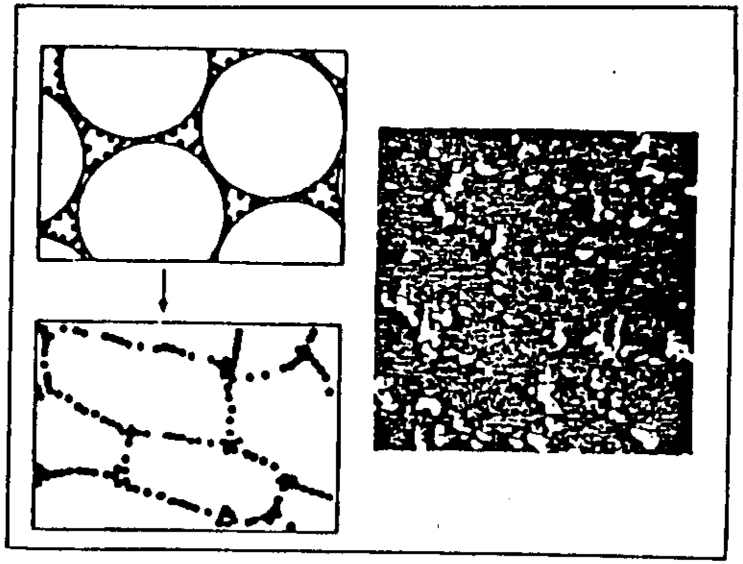


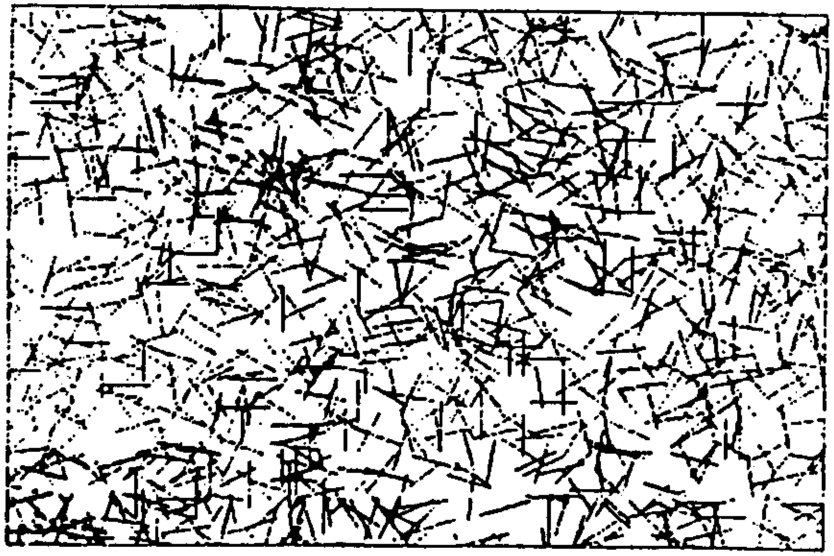
Formation of Mo particle chains in a Cu melt
(after Pötschke, D-1)



Possible structures in multidirectional solidification as a function of solidification rate, convection level, and particle size







Distribution of low volume percentage particles of short fibres

a) particles : no interconnection

b) fibres : network formation

c) skeleton formation due to linear chain agglomeration

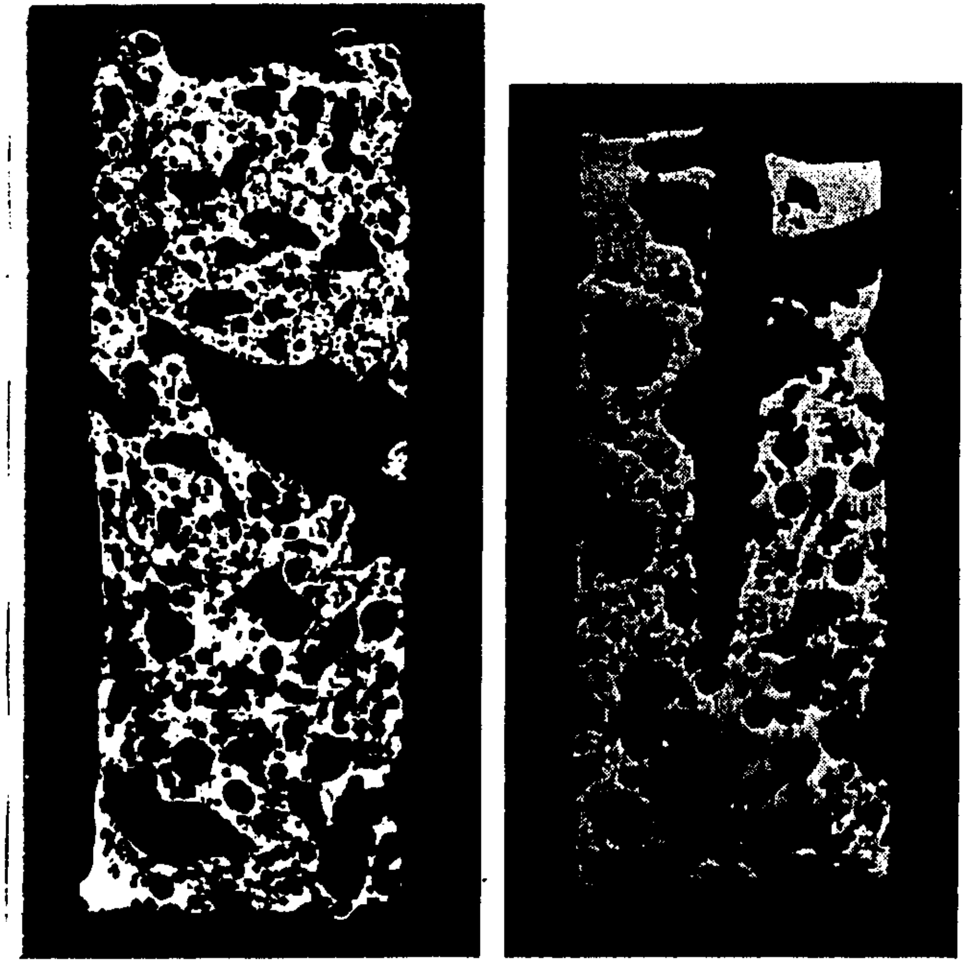


Fig. Flight sample (TEXUS VII, *left*) and 1-*g* reference sample (*right*) of a Fe - 4.3 % P alloy containing 0.13% nitrogen. Magnification 5 : 1 .

]

Controlled density materials (foams)

Inclusion of fine vapour "particles" into a metallic or ceramic matrix

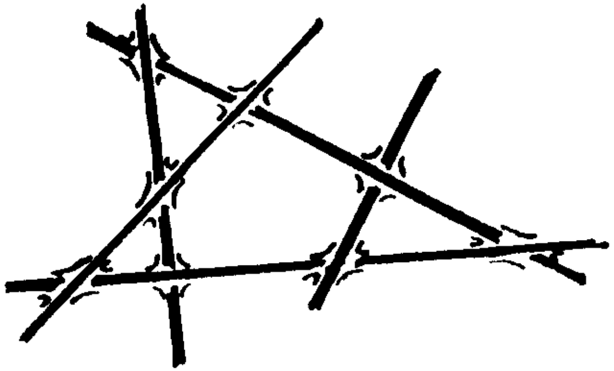
Experiment in μg and theoretical calculations: stability of foams (with liquid matrix) may not be sufficient in the absence of buoyancy and drainage.

* Surface forces lead to destabilization of polyhedral foams.
* Quick coalescence of gas bubbles in spherical foams
→ stabilization by surfactants or inclusion of solid phases (e.g. short fibres)

Ideas for µg:

* Production of hollow spheres with uniform and large diameters

* Connection and stabilization of fibre networks by liquid bridges



Industrial possibilities for space manufacturing of stiff and light-weight space structures

Medium Term Industrial Interests / Composites

- Controlled solidification of short fibre or particle reinforced composite materials

  * Management of casting process (iron, aluminium)

  * Influence of wetting behaviour on distribution of reinforcing phase

  * Determination of thermophysical properties for computer-modelling of solidification process

  * Solidification of three-dimensional structural components

PROBLEMS IN μ-G EXPERIMENTAL TECHNIQUES WITH STRONG IMPACT ON INTERPRETATION OF RESULTS

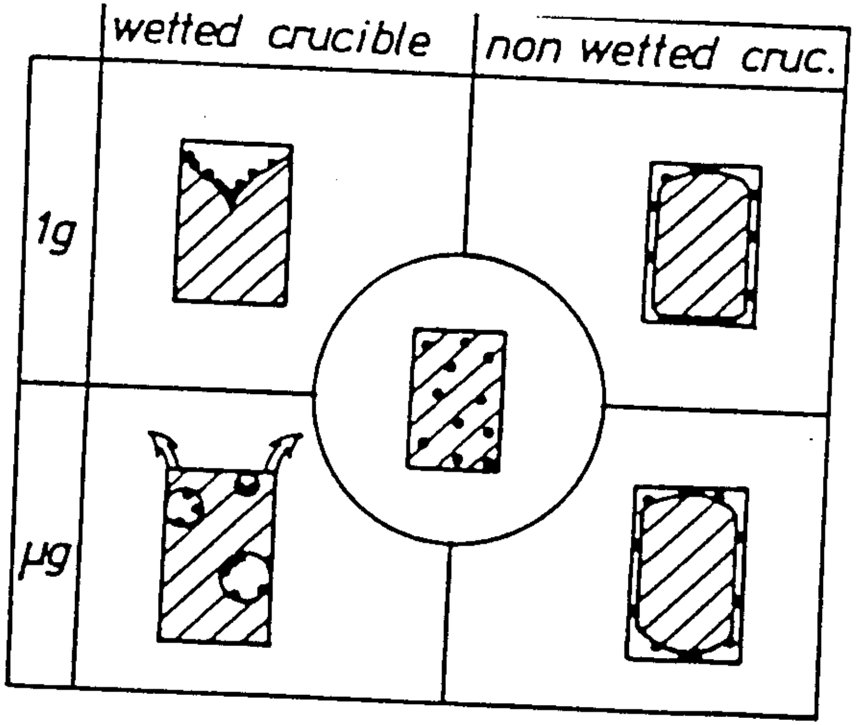
VOLUME CHANGE DURING MELTING AND SOLIDIFICATION

- FORMATION OF FREE SURFACES
  MARANGONI CONVECTION

- SEPARATION OF MELTS AND FORMATION OF CAVITIES

- FALSIFICATION OF INTENDED TIME-TEMPERATURE PROFILE
  TEMPERATURE GRADIENT
  COOLING RATE
  GROWTH RATE

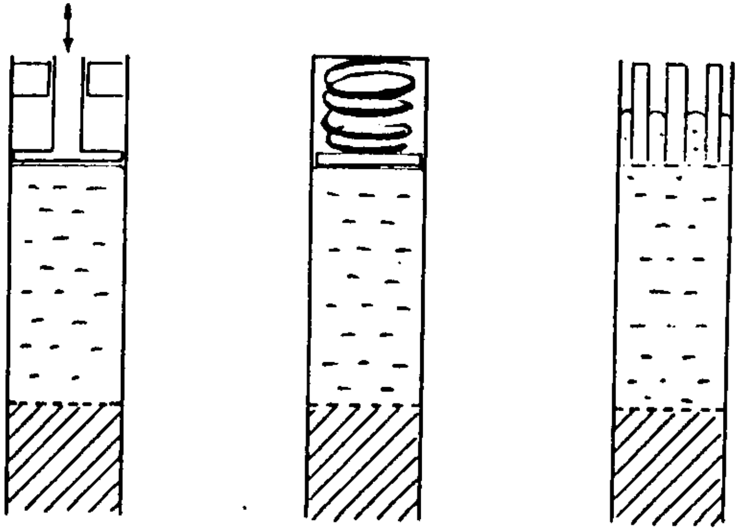
- DEMOLITION OF CRUCIBLES



Schematic representation of experimental 1-g and μ-g results showing the influence of wetting of the container on the behaviour of dispersed particles in a metallic melt

→ CONTROLLED MELTING AND SOLIDIFICATION

AUTOMATIC VOLUME CONTROL MECHANISM



FORMATION OF GAS BUBBLES

- CREATION OF NEW SURFACES

  MARANGONI EFFECTS, HEAT FLOW, TRAPPING OF PARTICLES, ETC.

- INTERNAL PRESSURE

  SPILLING OF MELT THROUGH CRACKS

  REACTION WITH CARTRIDGE

ORIGIN OF BUBBLES

- DIFFERENT SOLUBILITY LIQUID / SOLID E.G. H_2 IN AL
- CHEMICAL REACTION E.G. SiO_2 , Fe_2O_3 + C
- P/M PREPARATION OF SAMPLES

DIFFERENCE OF THERMAL BEHAVIOUR 1G / µ-G

- THERMAL GRADIENT IN MELT
- PULLING SPEED / GROWTH RATE
- CONVECTION IN PROCESS ATMOSPHERE

Directional solidification

Important parameters:

- temperature gradient
- solidification rate
- cooling rate

Metals and alloys:

G = 50 - 150 K/cm

V = 5 - 400 mm/h

Semiconductors:

G = 10 - 40 K/cm

V= 0.1 - 10 mm/h

Criteria for D.S. experiments:

- critical G/R (planar/cellular/dendritic)
- constant solidification rate
- flat phase boundary (slightly convex)

Options:

- in-situ control
- high rate quenching

Problems with cartridge design for HT Materials

- metals not suitable
  chemical reaction (Ni - Mo, Ta, W)

- internal coating is not state of the art

- ceramic crucibles

  * safety hazards
  * permeability for gases
  * difficult sealing

Necessary items for experiment design

- Consideration of process chamber/sample in total

- Calculation and optimization of heat fluxes within the systems heater - sample - cooler

- Knowledge of heat transfer between sample/cartridge and furnace resp. cooler

- Principal differences between materials of high and low thermal conductivity

  - high λ: T distribution determined mainly by the material
  - low λ: T distribution determined mainly by the arrangement of furnace/cartridge

General philosophy

- Avoid 'design by specification'.
- Develop hardware in close connection with experimenters (testing and optimization).
- Consider highest terrestrial standard.

Dia: 3 Turb. Schaufeln

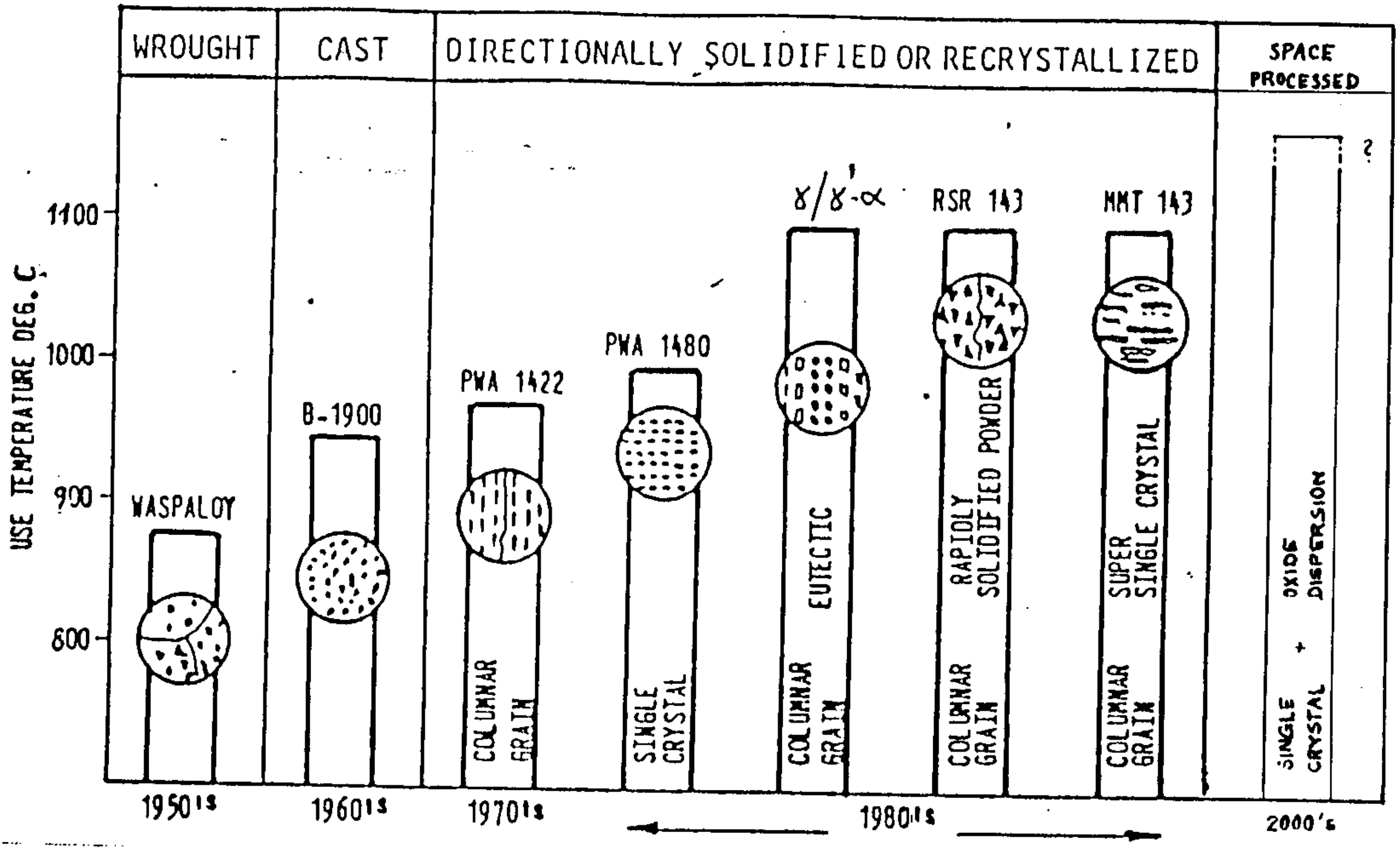


Bild 5: Einsatztemperaturen fortschrittlicher Turbinenschaufelwerkstoffe

Developments to increase permissable metal temperatures

Single Crystal Technolology	Mechanical Alloying	Rapid Solidification
high temp. low stress	◁- - - - - - - - - - - - - -▷	low temp. high stress
+ no grain boundaries	+ ceramic particles	
	- weak grain boundaries	- agglomeration of ceramic particles

solid state process

Future development directions:

"Change the melting point" ⟹ intermetallics

Ni_3Al (B), Ti_3Al-Nb

+ dispersions

RST + internal oxidation (Er_2O_3)

microgravity technology

O S I R I S

INTOSPACE

MAN
TECHNOLOGIE

Joint project

OSIRIS

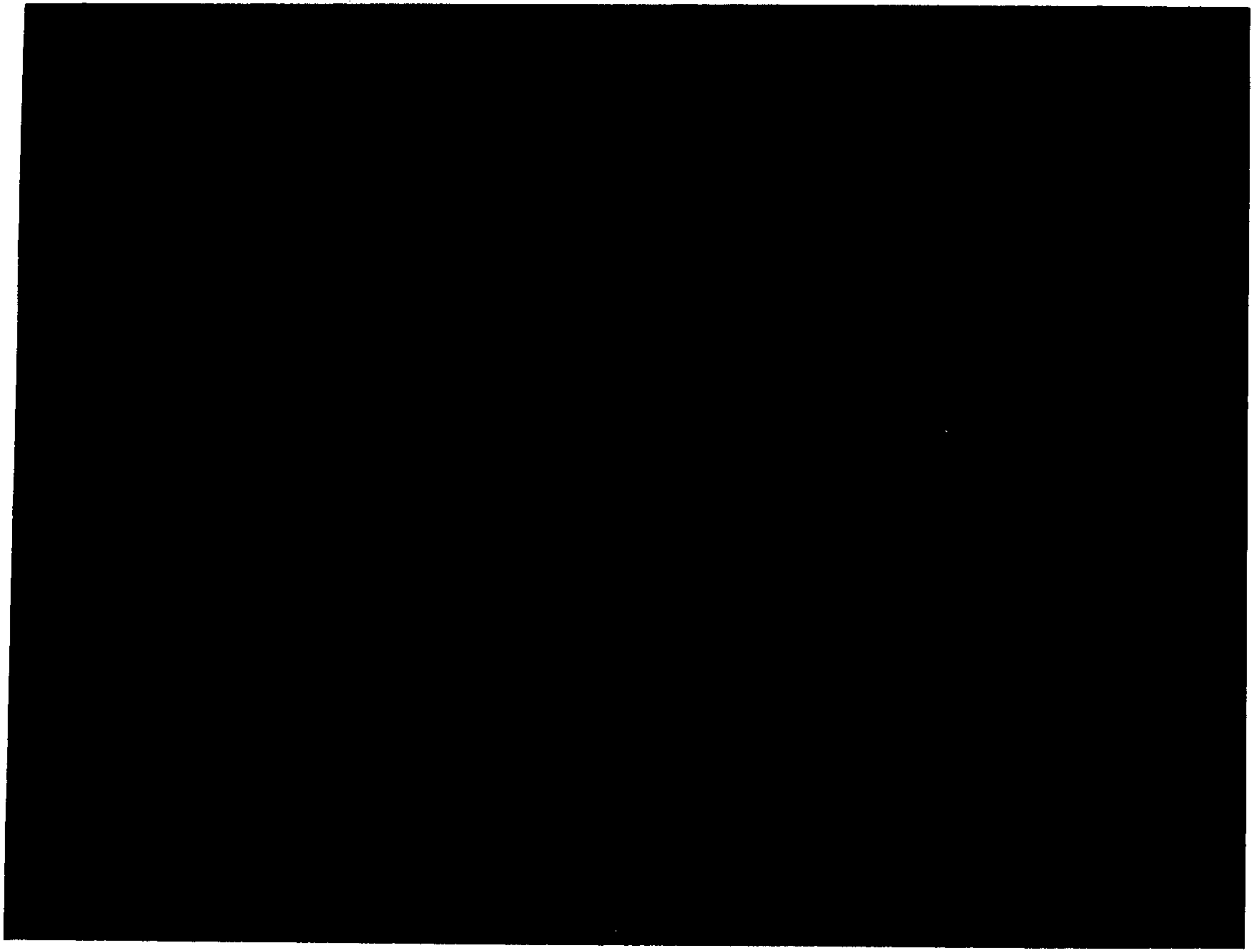
Oxide dispersion strengthened Single crystals

Improved by Resolidification In Space

Goals: Increase of high temperature creep strength by uniform distribution of very fine oxide particles in a single crystal superalloy matrix

Experimental investigations:

- stability of a particle suspension in a metallic melt
- interaction of particles with an advancing solidification front
- single crystalline solidification
- shaping of complex geometries (e.g. turbine blades)



Long Term Industrial Interests / Composites

* OSIRIS: Directional solidification of single cystal turbine blades reinforced by oxide particle dispersions

* Application of experience to higher melting point materials:

- Intermetallics (Ni Al, Ti Al)
- Ceramics

Aspects of industrial interests for Materials Processing in Space

- Investigations to improve terrestrial processes
- Preparation of reference samples and standards
- Commercial manufacturing of materials in space for industrial, medical and other applications
- Transfer of technology and know-how to non-space related applications

Preparation of High-Tc Superconductors

* Directional solidification of

Ag / Y-Ba-Cu-O
Pd / Y-Ba-Cu-O
Al (+ AgO) / Y-Ba-Cu-O

Effects of microgravity:

- Increase of uniformity of needle shaped crystals
- Investigation of segregation effects
  ("weak links" ⟶ low critical currents)

MICRO-G RESEARCH TOPICS	CONVENTIONAL PROCESSES	POSSIBLE NEW PROCESSES
• SOLIDIFICATION FRONT DYNAMICS	• INGOT CASTING	• IMPROVED SINGLE CRYSTALS OF VARIOUS TYPES
• SEGREGATION PHENOMENA (S-L INTERFACE INTERACTIONS WITH FOREIGN INCLUSIONS)	• CONTINUOUS CASTING • CRYSTAL GROWTH • NEAR NET-SHAPE CASTING	• DISPERSOID MATERIALS
• IMMISCIBLE ALLOYS	• CONTINUOUS SOLIDIFICATION PROCESSES	• PROCESSING EXTREMELY IMMISCIBLE ALLOYS (AL-PB)
• NUCLEATION • RAPID SOLIDIFICATION • UNDERCOOLED MELTS	• AMORPHOUS AND PARTIALLY CRYSTALLIZED FOILS • MELT PARTICULARIZATION	• LARGE VOLUME AMORPHOUS, METASTABLE AND/OR FINE-GRAINED ALLOYS • AUTONOMOUS DIRECTIONAL SOLIDIFICATION
• "LARGE INGOTS", SHAPE GIVING PROCESSES • UTILIZING SPREADING ON SURFACES	• CONTAINERLESS MELTING AND SOLIDIFICATION • SHAPE CASTING	• SKIN TECHNOLOGY • IMPROVED MICRO-STRUCTURES OF VARIOUS TYPES
• NUMERICAL MODELING WITH RESPECT TO OPTIMIZATION AND PREDICTABILITY	• CONTINUOUS CASTING • SHAPE CASTING	• ALL SOLIDIFCATION TECHNOLOGIES • SYSTEM FURNACE-INGOT OR SAMPLE
• DEVELOPMENT AND CONSTRUCTION OF SPECIAL (DEDICATED) EQUIPMENT	• FURNACES • DIAGNOSTICS • MIXERS AND POSITIONERS • ACCELEROMETERS	MICRO-G DEDICATED • FURNACES • MEASURING EQPMT. • MIXERS • POSITIONERS • ACCELEROMETERS

Directional solidification of Composite Materials

- In-situ composites: eutectics
  monotectics
  immiscible alloys

- Artificial composites: dispersion materials
  particle composites
  short-fiber composites

- Controlled density materials: foam metals
  hollow spheres

- Combination of different mechanisms:
  e.g. short fiber reinforced foam materials