N91-21339

Containerless Processing of Undercooled Melts

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All practical solidification processes involve some level of melt undercooling. Usually in bulk liquids crystallization is initiated at a heterogeneous nucleation site at low undercooling. The realization of appreciable levels of liquid undercooling requires some control over the kinetics of crystal nucleation. One level of control is available in containerless processing where the capability to melt and solidify samples without a container removes a major source of impurities and heterogeneous nucleation sites which can be effective in promoting large undercooling and in studying other potential nucleants. This is a critical advantage offered by containerless processing. On earth containerless processing may be achieved for small samples by electromagnetic, acoustic or electrostatic levitation or by dropping small molten droplets through a long evacuated tube and allowing them to solidify during free-fall. Although ground based methods are useful, they have limitations. Levitation approaches induce melt disturbances which may influence nucleation and limit the attainable undercooling. During drop tube processing it is difficult to obtain a continuous and accurate measurement of sample temperature during free-fall. Moreover, all ground based methods are restricted to small samples. The microgravity environment offers a unique opportunity for containerless processing of large liquid samples with negligible melt disturbance and continuous temperature measurement throughout processing. One use of this approach is to allow for physical property measurements that are not accessible by usual techniques. Perhaps the most important potential for microgravity containerless processing lies in the significant structural control to develop distinct microstructures and metastable phases during solidification at high undercooling. In order to realize this potential ground based experiments are required to establish the key processing parameters such as melt superheat, fluxing, thermal cycling and sample atmosphere that control undercooling and nucleation of different structures. A ground base experimental experience is also crucial to the development of a suitable microgravity experimental facility and to the interpretation of microgravity test results.

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UNDERCOOLING

. WHAT IS IT?

$T_m - T$

. HOW DOES IT DEVELOP?

Crystallization rate limitations

. WHY IS IT IMPORTANT?

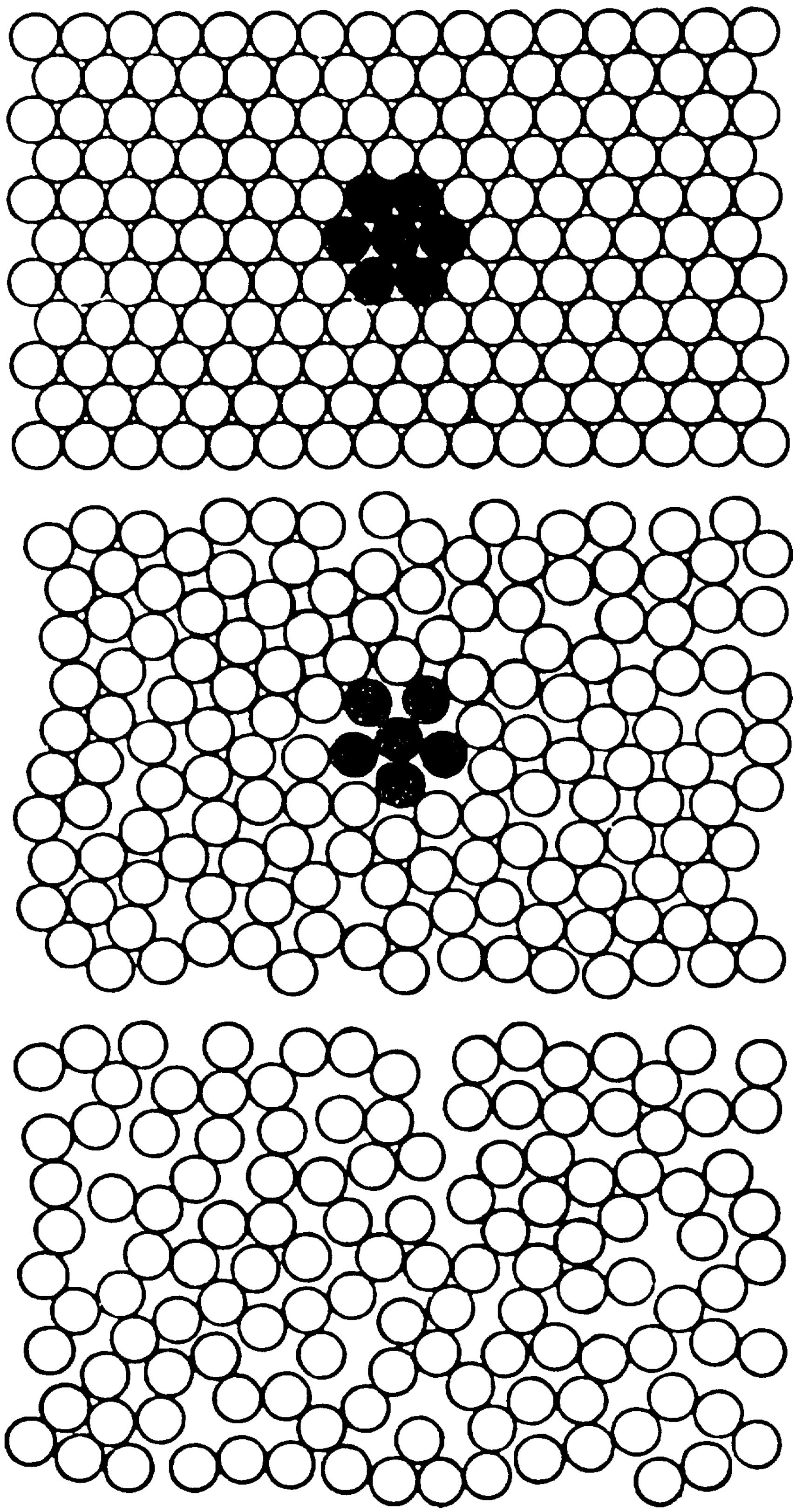
Controls initial solidification path

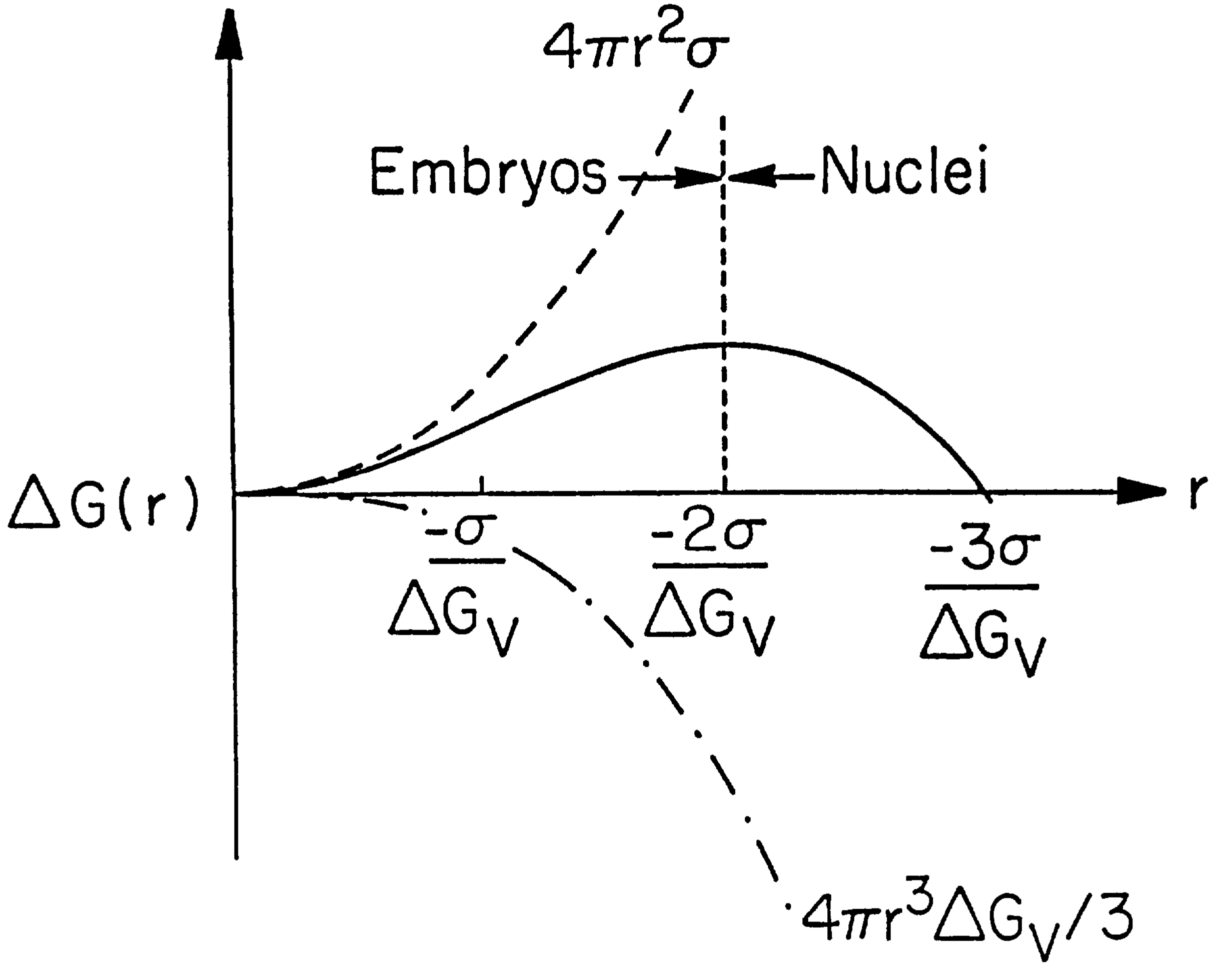
UNDERCOOLED MELTS

* General Kinetic and Thermodynamic Features of Metastability and Undercooling

* Containerless Processing - Experiment and Analysis
    - Kinetic Studies
    - New Structures
    - Process Control

* Open Issues





$4\pi r^2\sigma$
Embryos
Nuclei
$\Delta G(r)$
r
$\frac{-\sigma}{\Delta G_V}$
$\frac{-2\sigma}{\Delta G_V}$
$\frac{-3\sigma}{\Delta G_V}$
$4\pi r^3 \Delta G_V/3$

DIFFICULTIES IN ACHIEVING EQUILIBRIUM

* Equilibrium diagram gives stable equilibrium

* Metastable equilibrium results when a system is subjected to constraints
    - Coherency
    - Stable phase missing or metastable phase present
    - Sluggish kinetics

* Metastable equilibrium is a reversible equilibrium

* Metastable equilibrium information can be useful in phase diagram evaluation
    - Test thermodynamic models

* Other non-equilibrium information
    - T_0 curve

To Optimize Undercooling...

1. High degree of particle size refinement and narrow size distribution

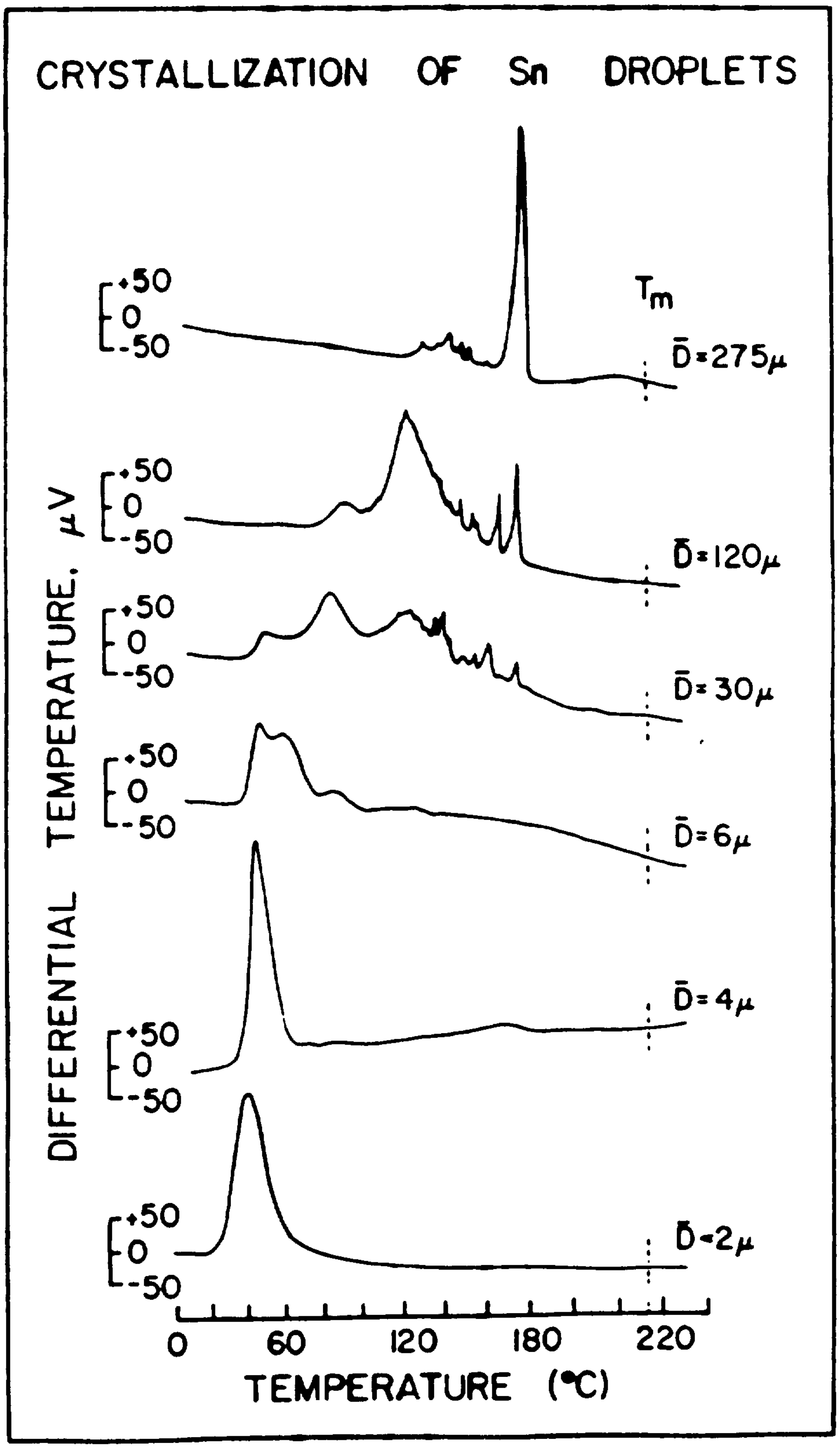
2. Non-catalytic surface coating
   -wet liquid

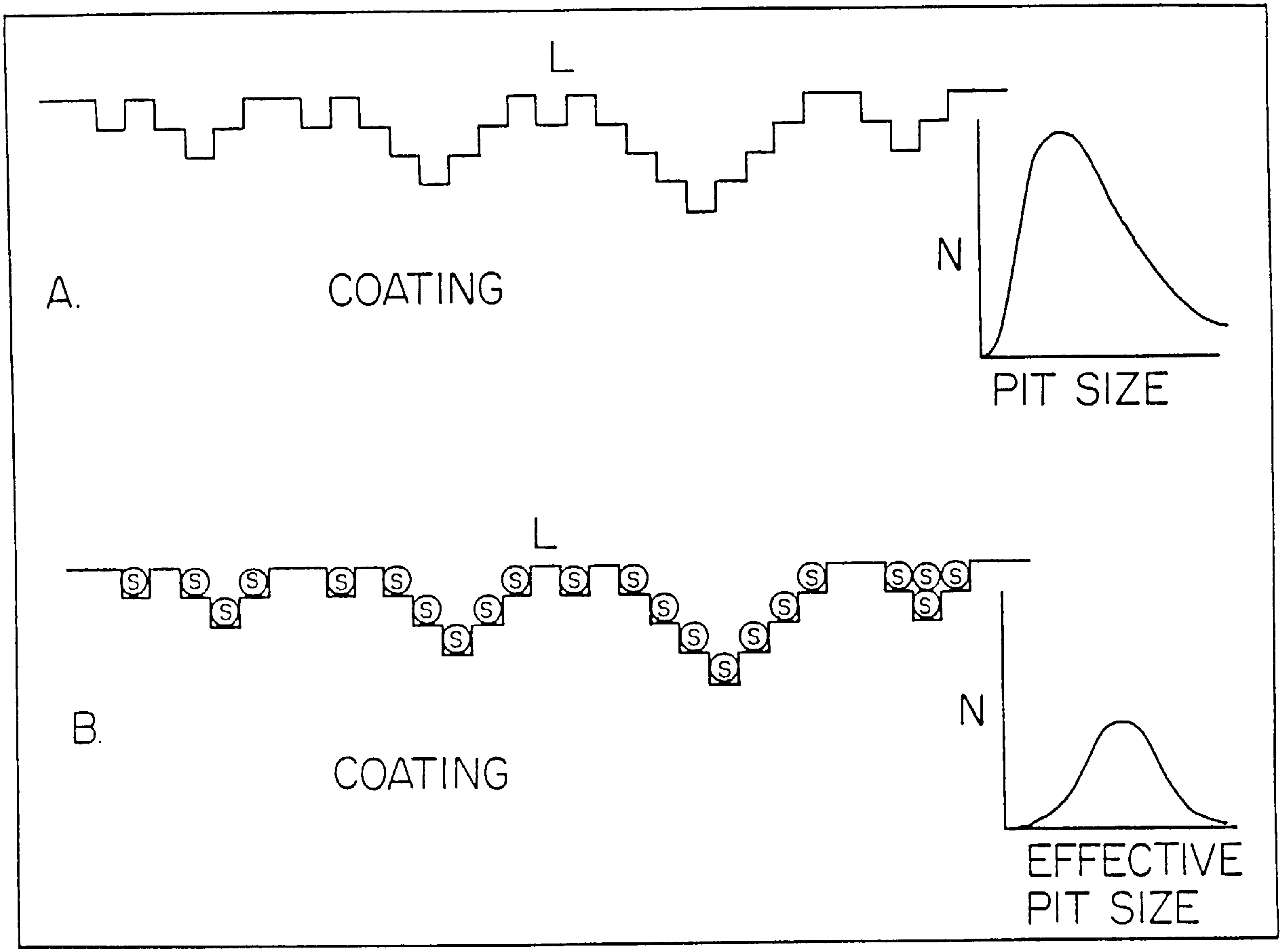
3. Uniform surface coating

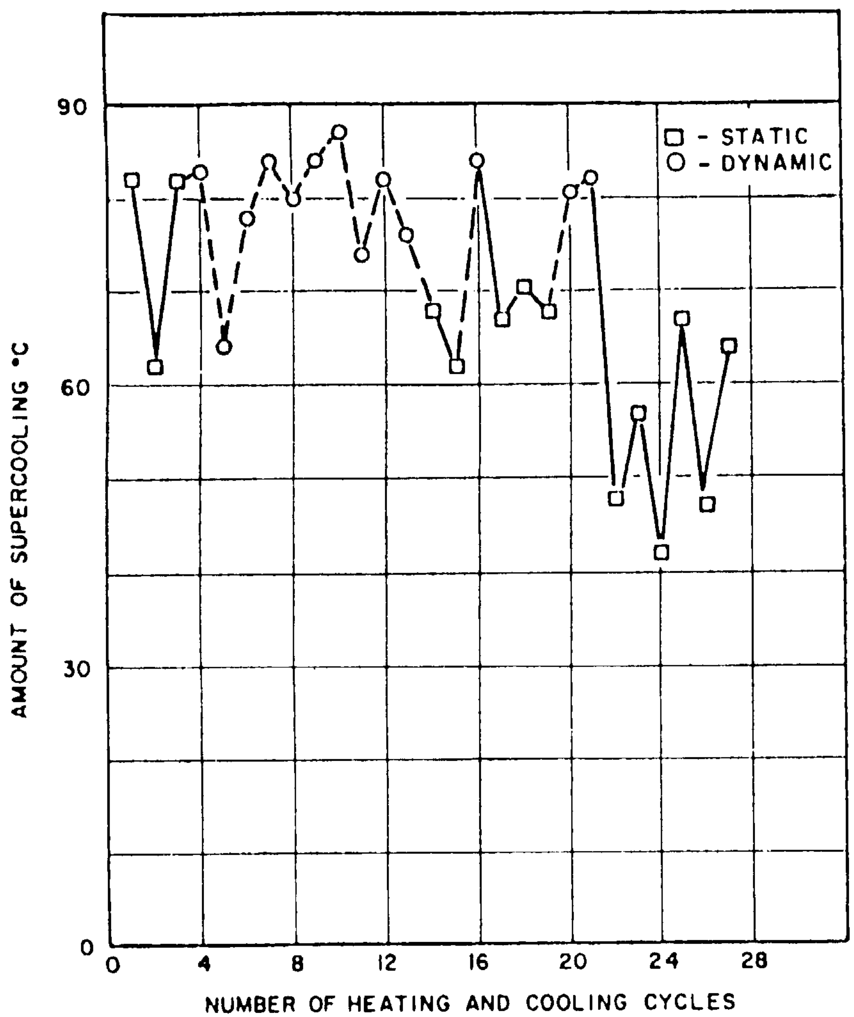
4. Purity: specific effects

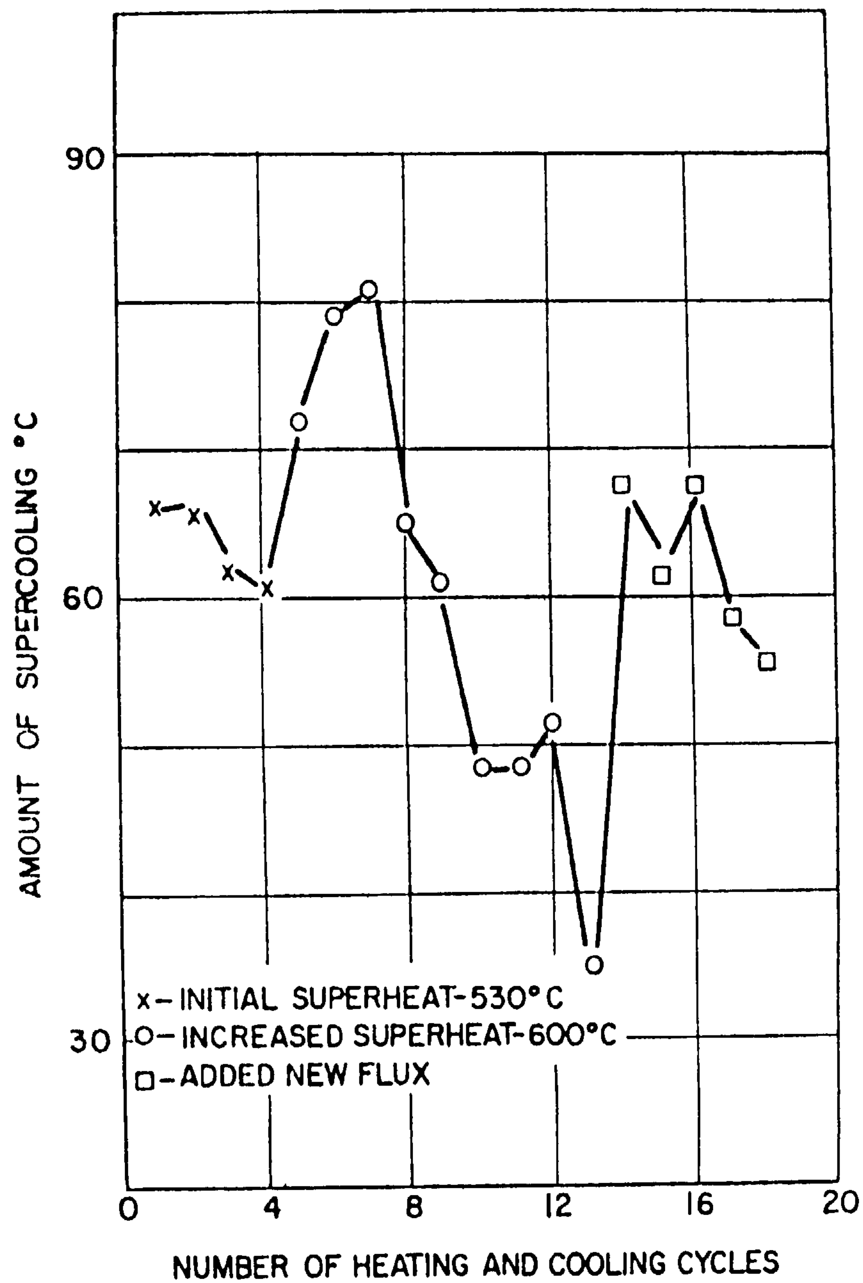
5. Perserverance

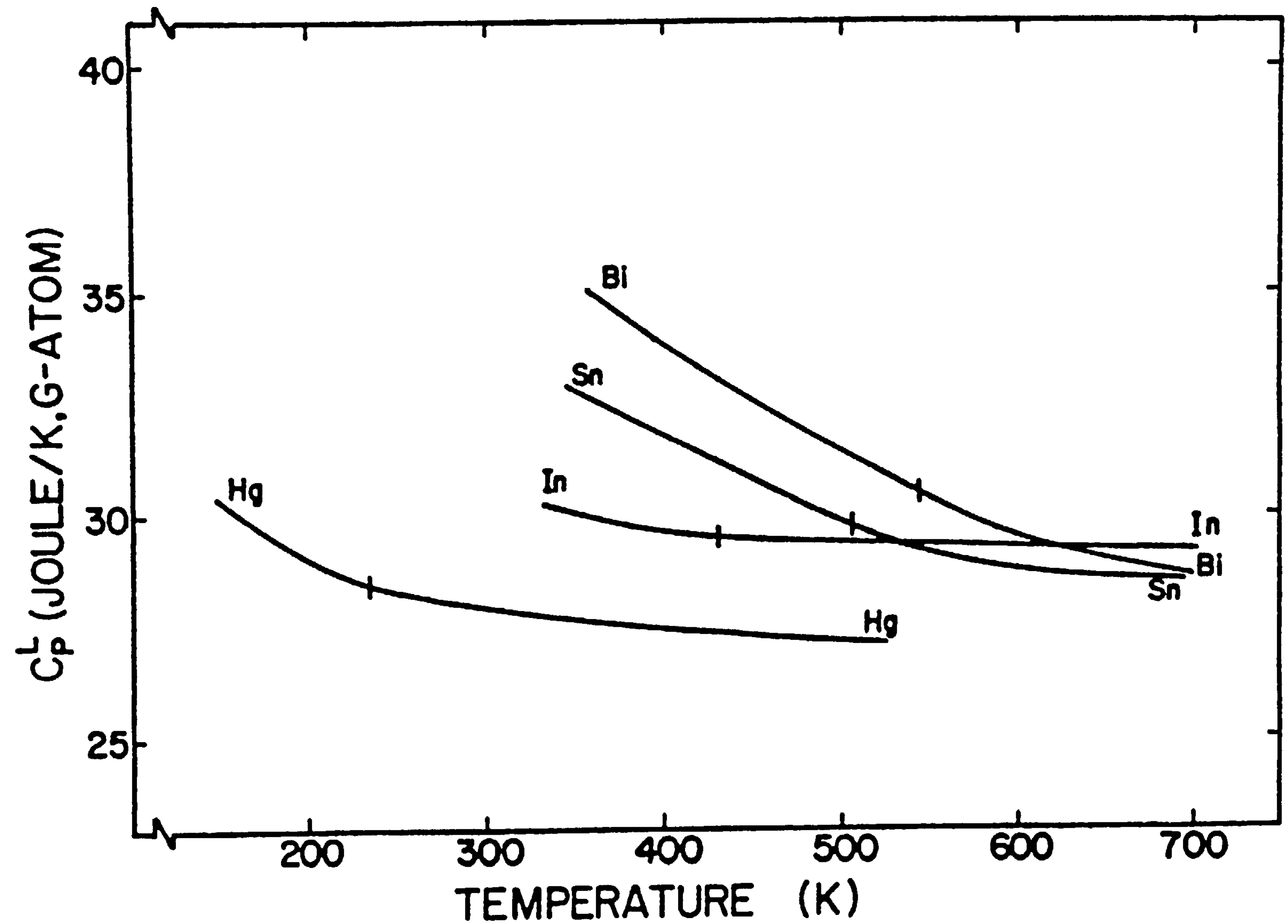
6. Increased cooling rate is often useful

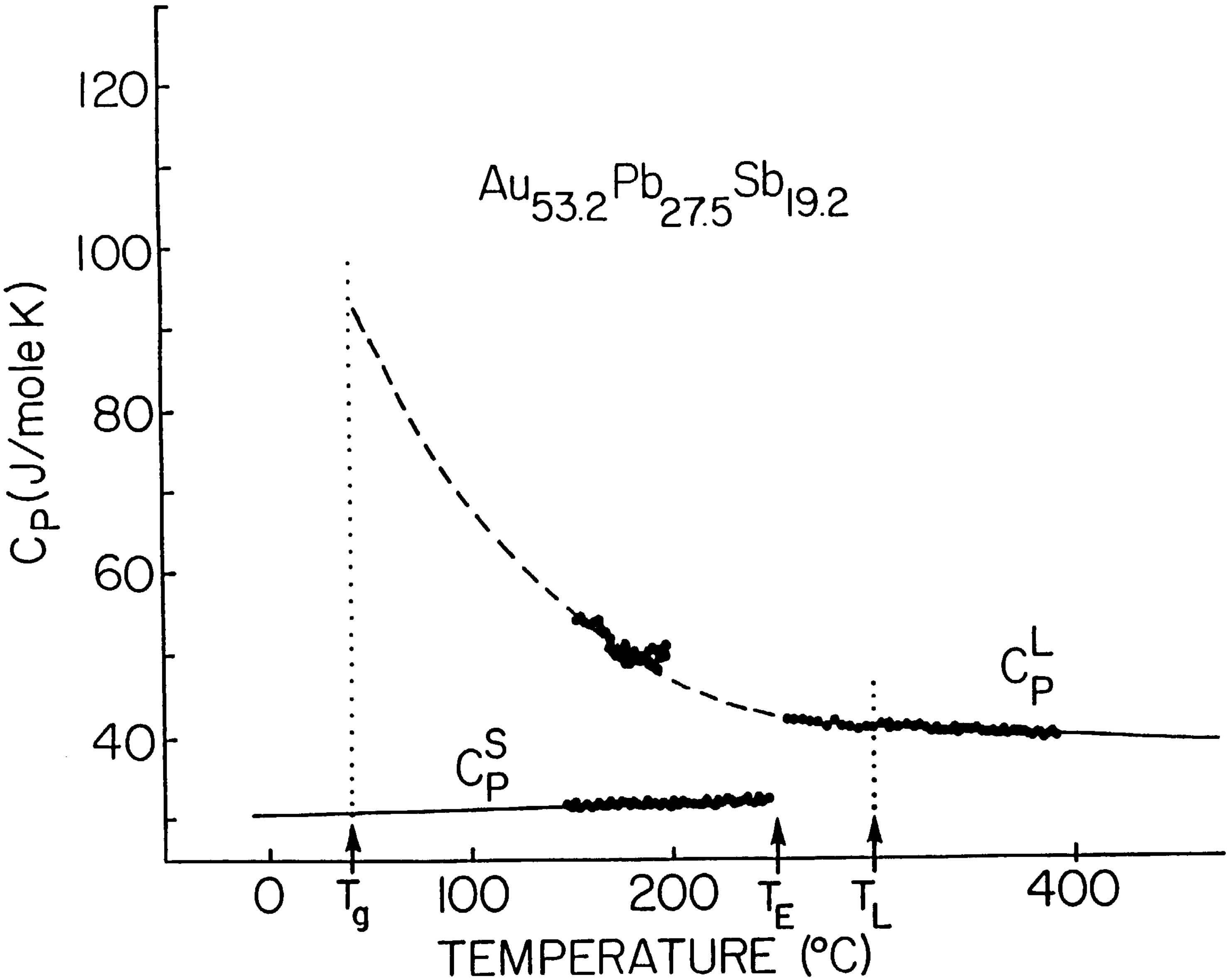

CRYSTALLIZATION OF Sn DROPLETS
DIFFERENTIAL TEMPERATURE, μV
+50
0
-50
Tm
D̄=275μ
D̄=120μ
D̄=30μ
D̄=6μ
D̄=4μ
D̄<2μ
0
60
120
180
220
TEMPERATURE (°C)

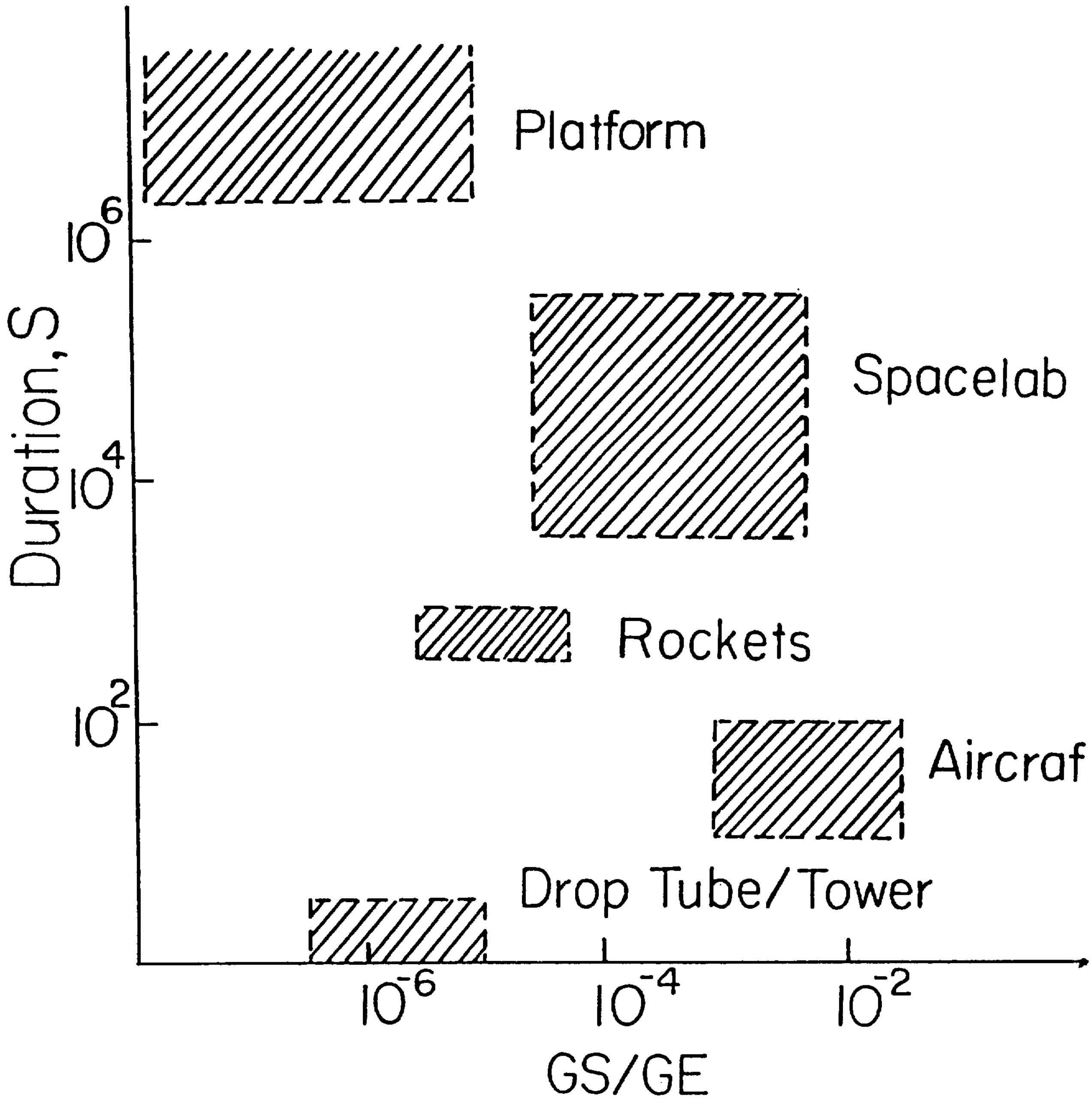

L
A.
COATING
N
PIT SIZE
L
S
B.
COATING
N
EFFECTIVE
PIT SIZE


90
60
30
0
AMOUNT OF SUPERCOOLING °C
□ - STATIC
○ - DYNAMIC
0
4
8
12
16
20
24
28
NUMBER OF HEATING AND COOLING CYCLES

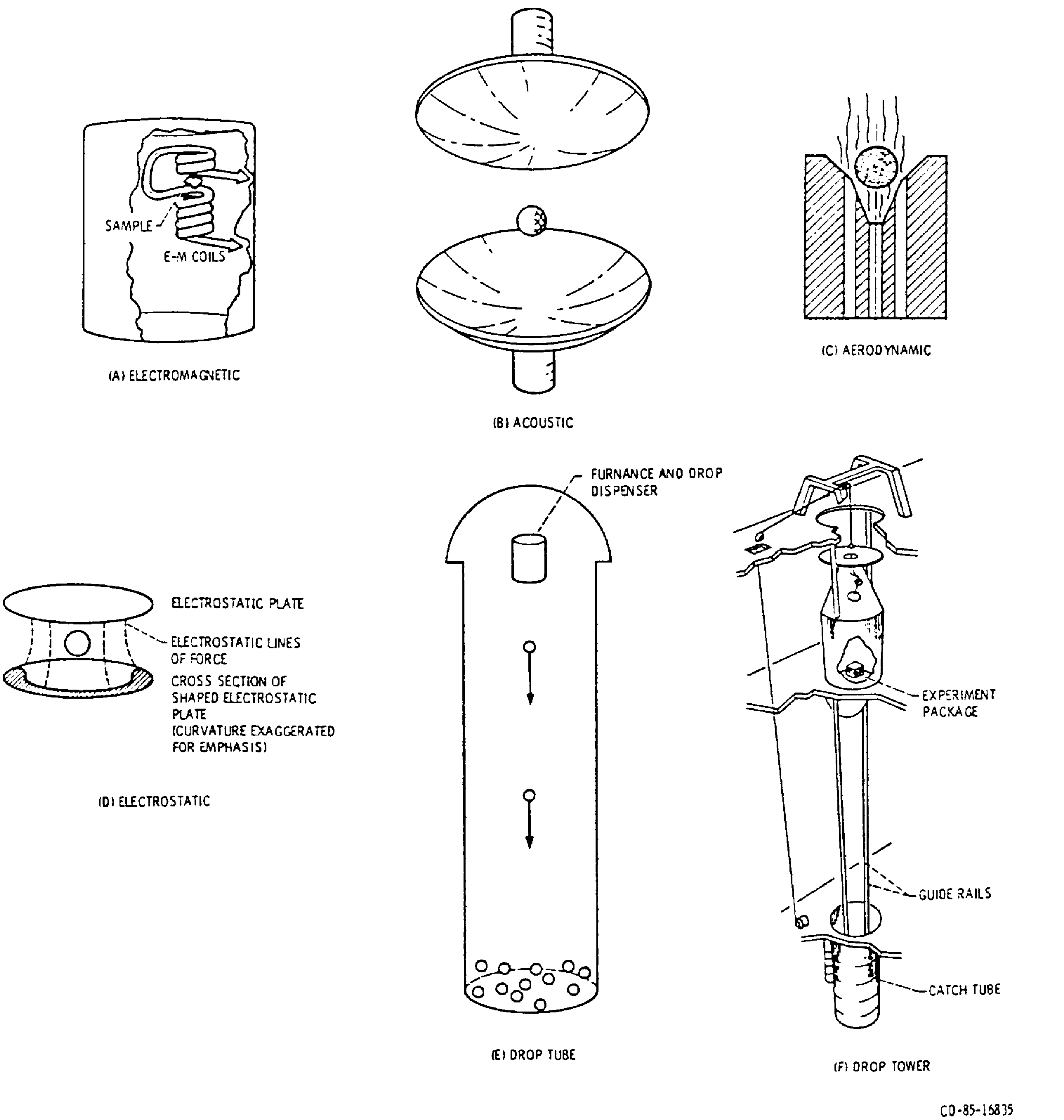

90
60
30
AMOUNT OF SUPERCOOLING °C
x – INITIAL SUPERHEAT-530°C
○ – INCREASED SUPERHEAT-600°C
□ – ADDED NEW FLUX
0
4
8
12
16
20
NUMBER OF HEATING AND COOLING CYCLES


Bi
Sn
In
Hg
In
Bi
Sn
Hg
40
35
30
25
200
300
400
500
600
700
TEMPERATURE (K)
C_p^L (JOULE/K,G-ATOM)


$Au_{53.2}Pb_{27.5}Sb_{19.2}$
C_P (J/mole K)
120
100
80
60
40
C_P^L
C_P^S
0
T_g
100
200
T_E
T_L
400
TEMPERATURE (°C)


Platform
Spacelab
Rockets
Aircraft
Drop Tube/Tower
Duration, S
10^6
10^4
10^2
10^{-6}
10^{-4}
10^{-2}
GS/GE

B-5. CONTAINERLESS PROCESSING TECHNIQUES



-<u>Containerless Processing Potential</u>

* Minimize Reactivity
* Avoid Crucible Induced Nucleation, but...
* Possibility of Ultrapure Melts (especially surface)
* Avoid Vibration Effects

-<u>Microgravity and Containerless Processing</u>

* Large Sample Possible
* Vacuum
* Sample Positioning
* Minimize Fluid Flow Effects

-<u>Undercooled Melts</u>

* Refined Microstructure
* Suppressed Segregation
* New Phases - Metastable (glass)
* Control Phase Selection

- Containerless Processing/Solidification of Undercooled Melts

* Identify and control key processing variables (superheat, sample size, purity, atmosphere, cooling rate)

* Heat flow analysis

* Develop temperature measurement

* Examination of sample surface and relation to undercooling

* Solidification kinetics

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* Sample size scale-up

* Influence of melt vibration and flow

Containerless Processing and Microgravity

1) The microgravity environment of space allows for containerless processing of extended duration.

2) Microgravity processing can allow for the study of the under-cooling and solidification response in pure, uncoated samples.

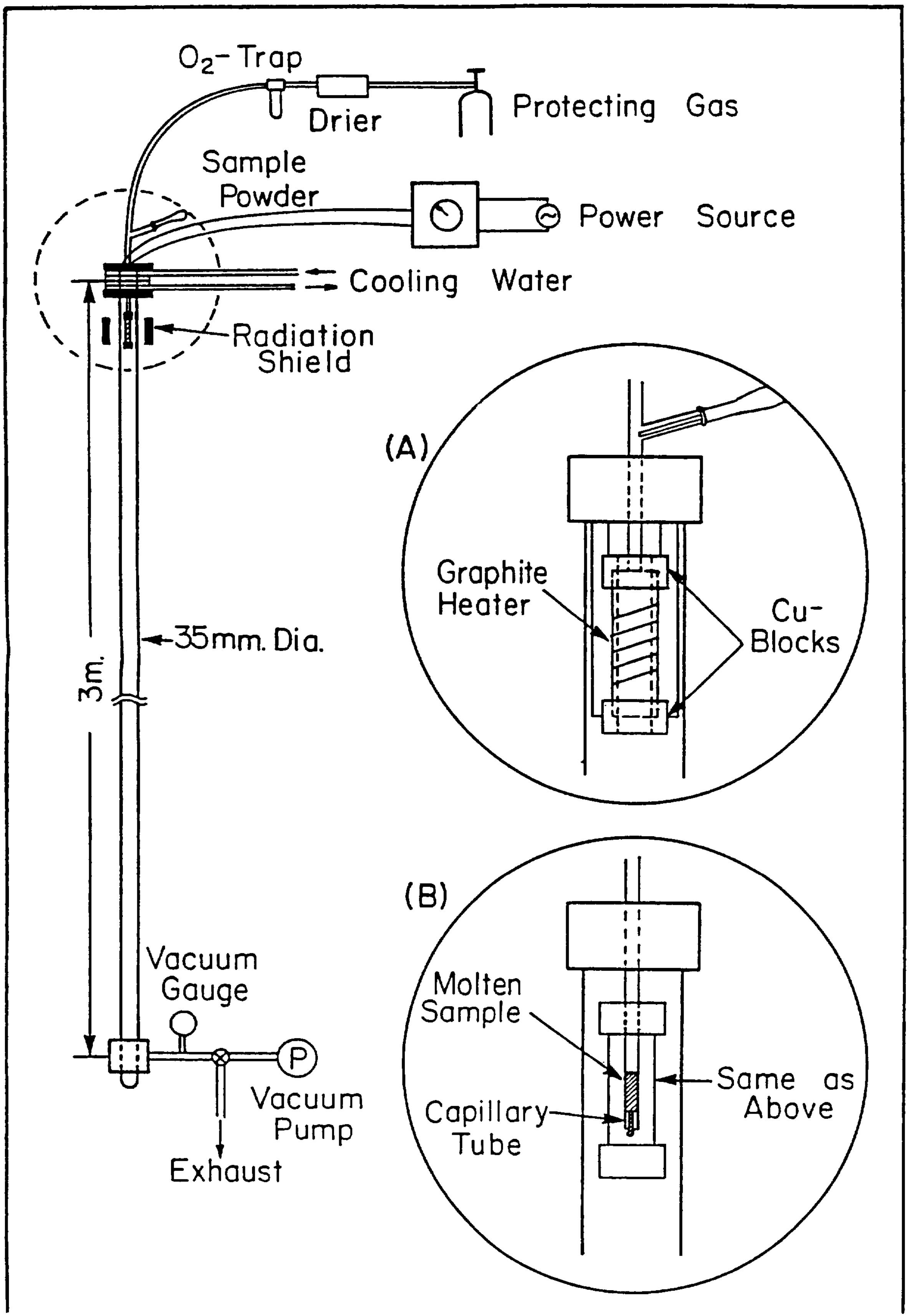
3) With extended duration treatment the influence of controlled coating reactions on undercooling response may be evaluated for application ot the development of upscaled sample volumes.

4) The experience from ground-based containerless processing work will provide the background that is needed to interpret, evaluate and maximize solidification structure control during microgravity treatment.

OBJECTIVES:

Develop and Test Concepts for Microgravity Experiments

* Containerless Processing
* Solidification of Undercooled Melts
* Microstructural Evolution



O_2- Trap
Drier
Protecting Gas
Sample
Powder
Power Source
Cooling Water
Radiation
Shield
35mm. Dia.
3m.
Vacuum
Gauge
P
Vacuum
Pump
Exhaust
(A)
Graphite
Heater
Cu-
Blocks
(B)
Molten
Sample
Capillary
Tube
Same as
Above

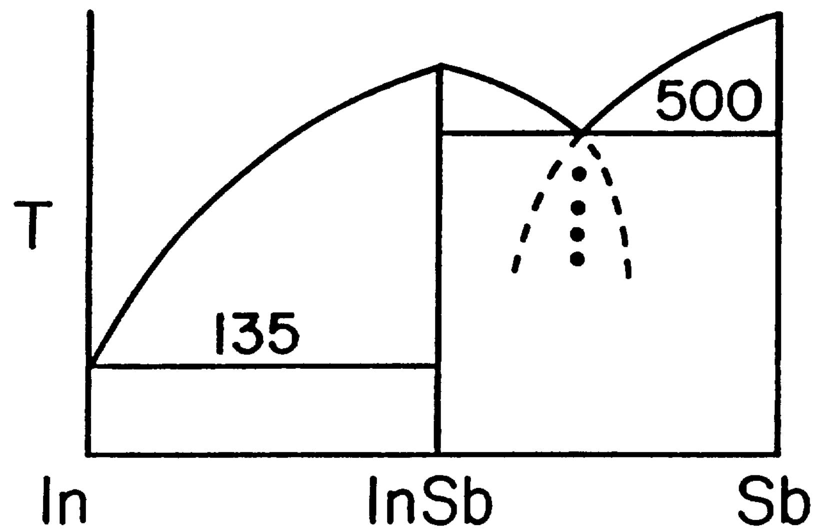
Evaluation of Liquid Undercooling

1) microstructural scale
   a) eutectic alloy

2) metastable phase formation
   a) amorphous solid
   b) Fe-Ni: bcc vs. fcc

3) heat flow analysis with experimental verification

Eutectic Solidification



$\Delta T = k_1 \lambda v + k_2/\lambda$ (Reg. Growth: $\Delta T_k \simeq 0$)

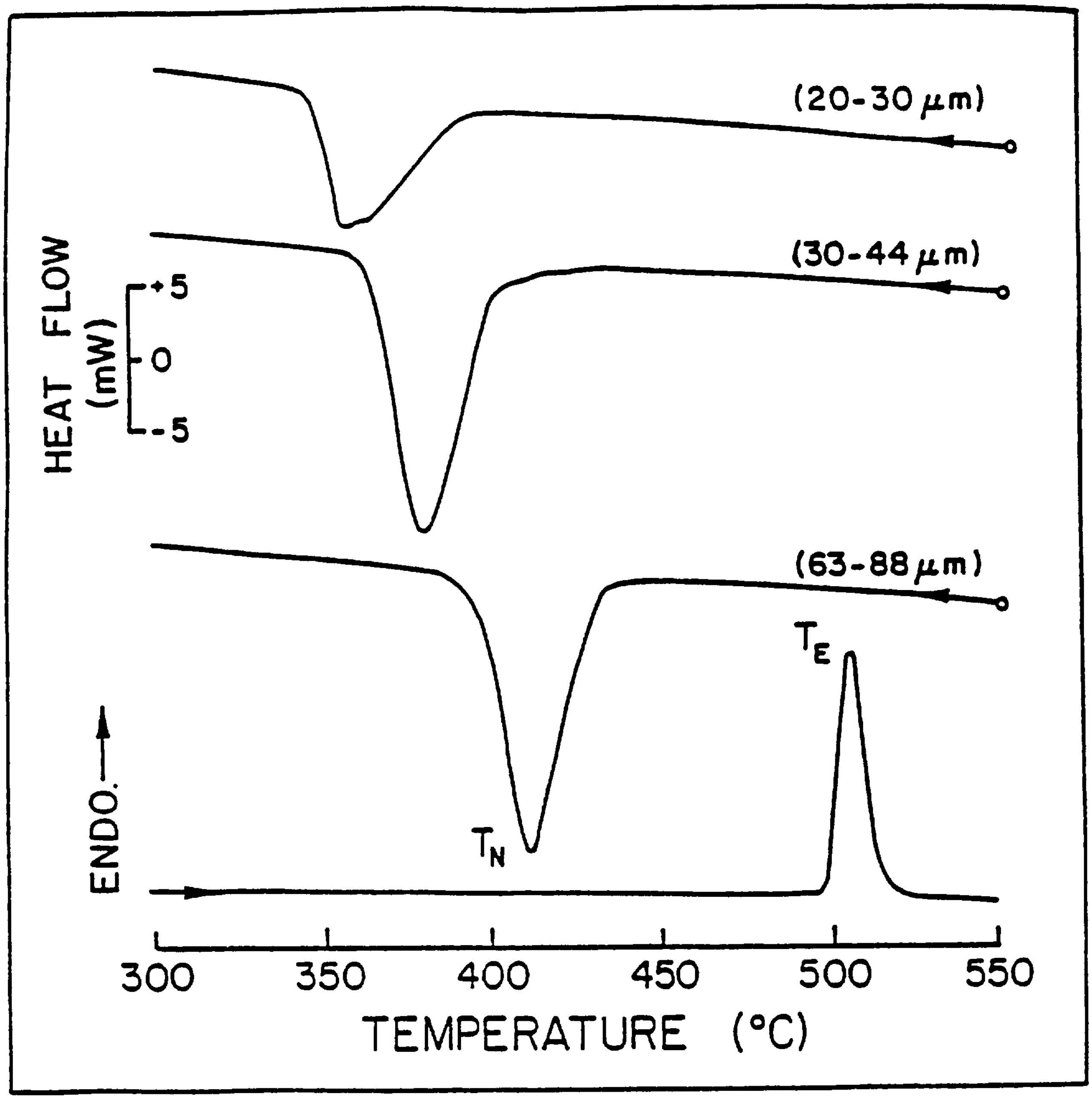
$\lambda^2 v = C_1$; $T^2/v = C_2$; $\Delta T \lambda = C_3$

For InSb-Sb (f-f, $T_k \neq 0$, branching limit)

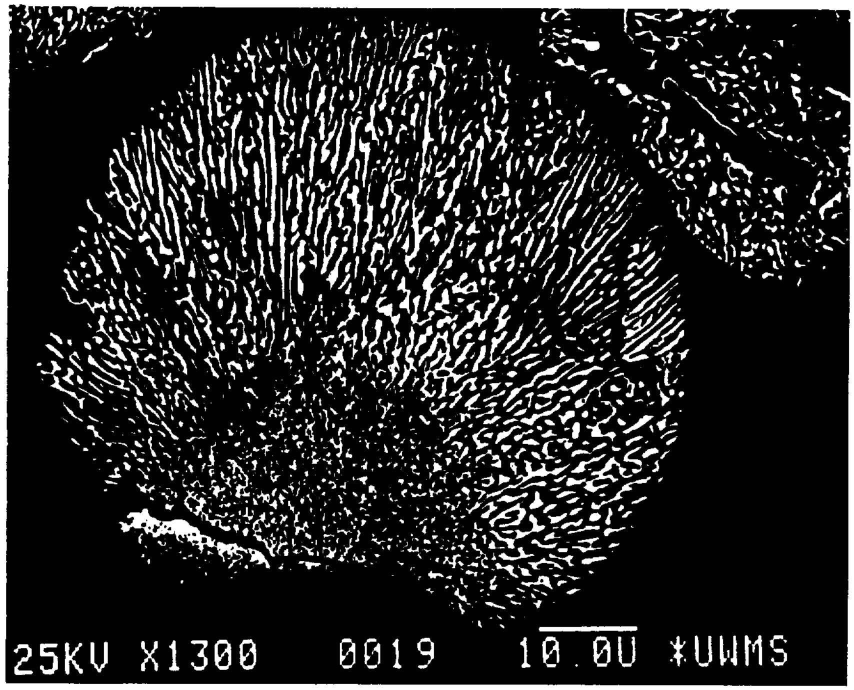
$\ln v = -4.16 - 2.09 \ln \lambda$ (Measured in D.S. Liebmann and Miller)

$\ln \lambda = 14.94 - 1.56 \ln \Delta T$ (Measured in droplet ΔT at onset - i.e. T_n)

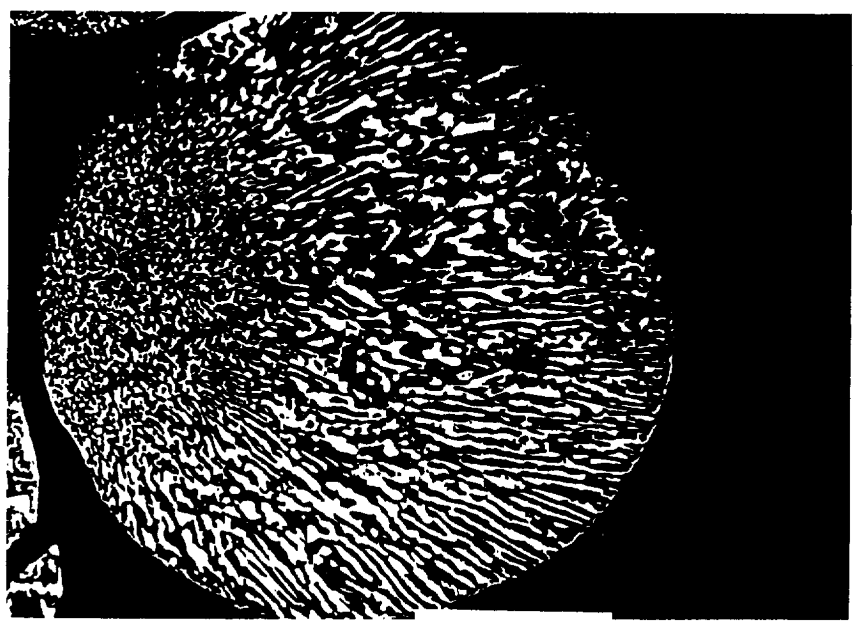
λ onset $\rightarrow \Delta T \rightarrow v$



(20-30 μm)
(30-44 μm)
(63-88 μm)
HEAT FLOW (mW)
+5
0
-5
ENDO.
T_E
T_N
300
350
400
450
500
550
TEMPERATURE (°C)

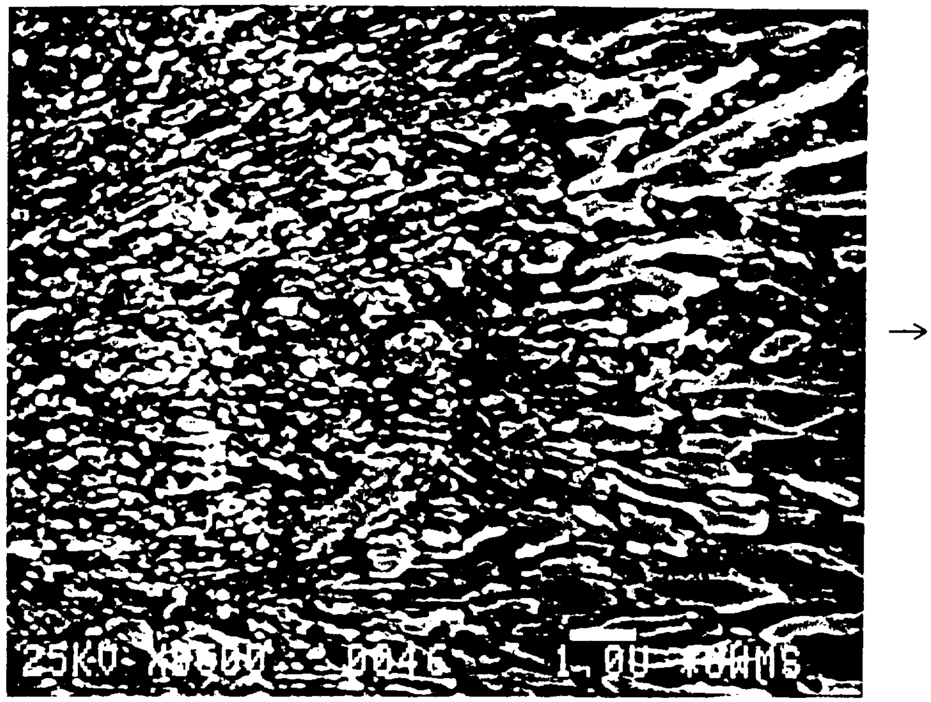


(a)

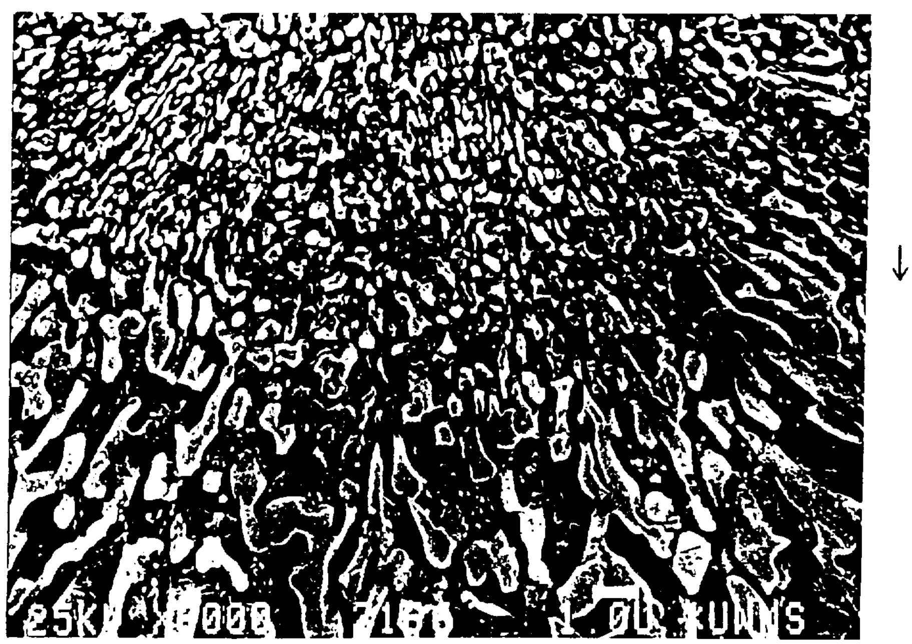


(b)

Figure 51. SEM micrographs showing the solidification structure following DSC Processing.
(a) 1300X. (b) 2600X.

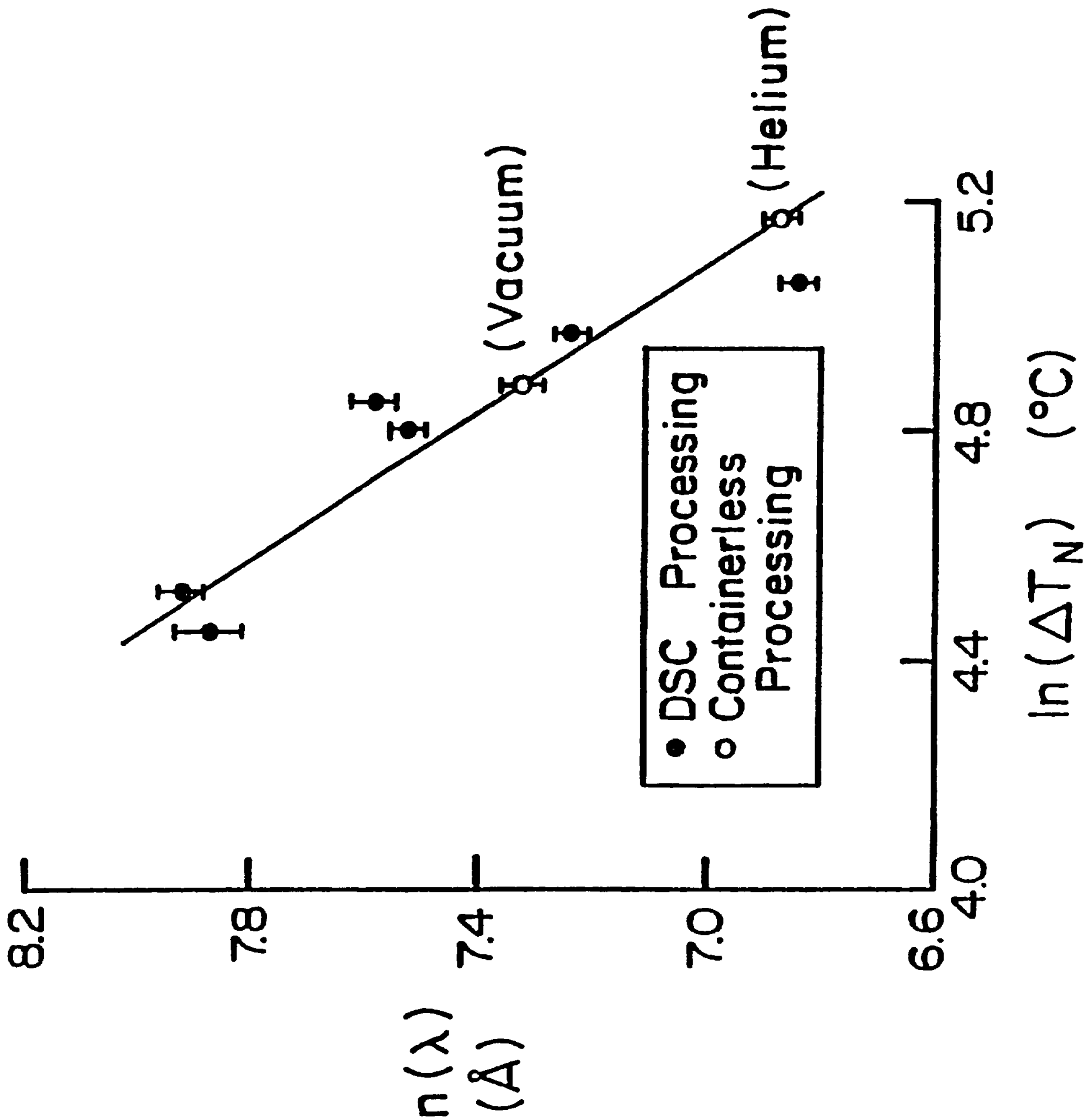


(a)

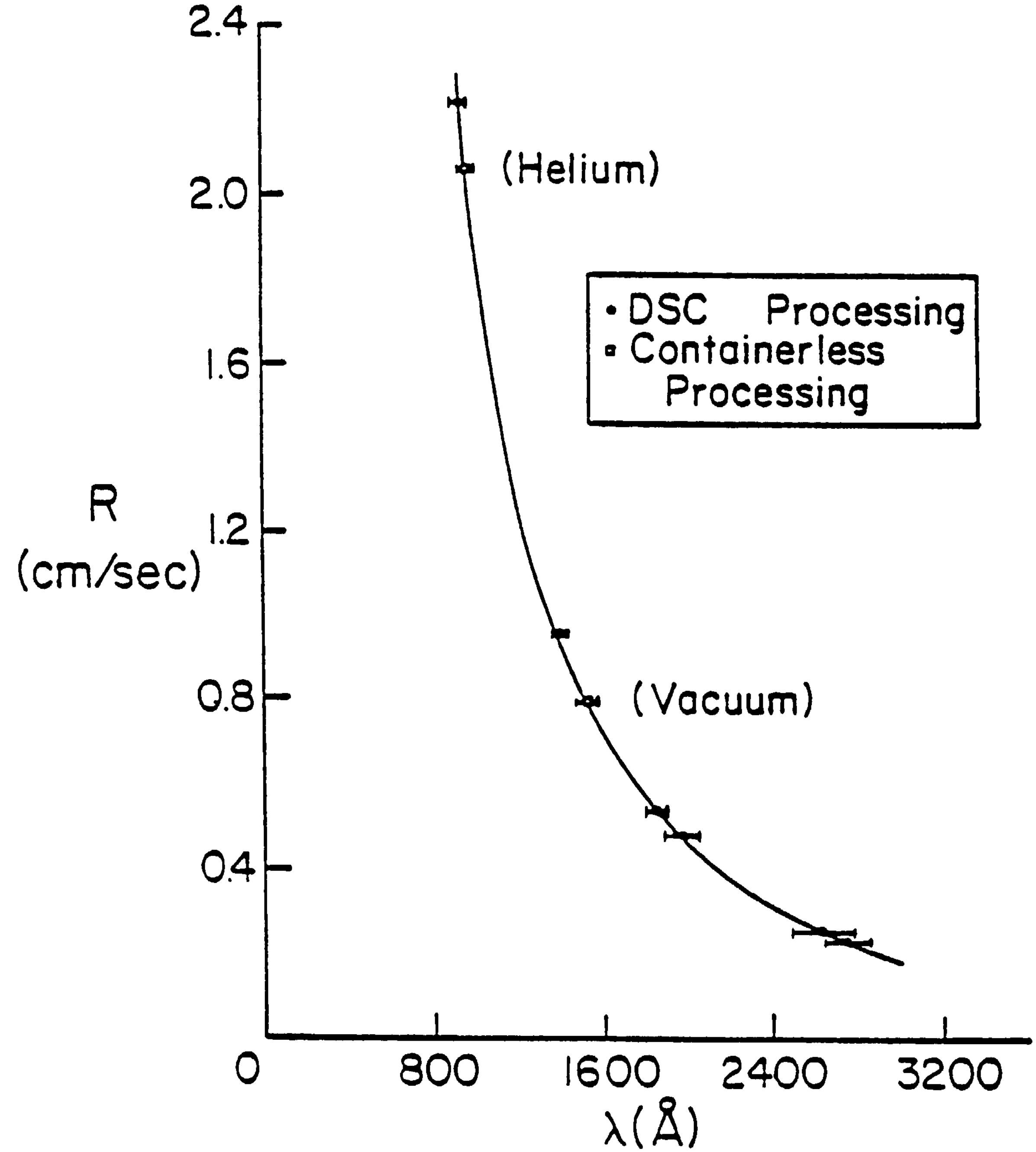


(b)

Figure 53. SEM micrographs illustrating the transition from a rod to lamellar morphology. (a) 8600X. (b) 6000X.

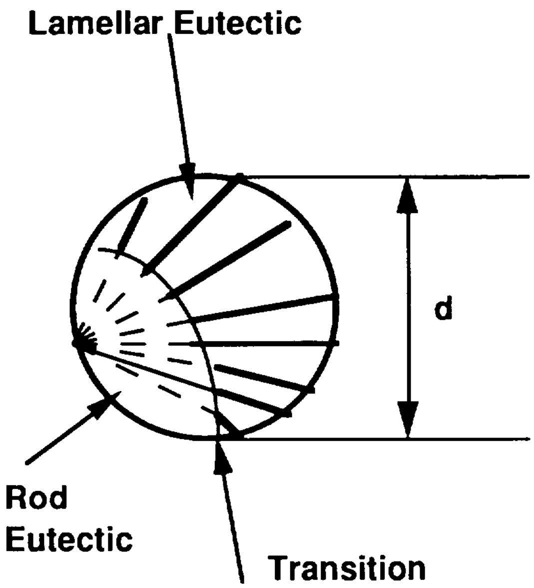


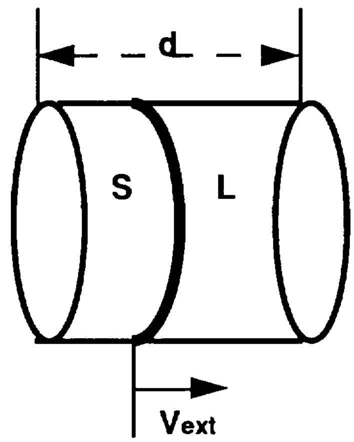
ln(λ)
(Å)
8.2
7.8
7.4
7.0
6.6
4.0
4.4
4.8
5.2
ln(ΔT_N) (°C)
(Vacuum)
(Helium)
• DSC Processing
o Containerless Processing


2.4
2.0
1.6
1.2
0.8
0.4
0
R
(cm/sec)
800
1600
2400
3200
λ(Å)
(Helium)
(Vacuum)
• DSC Processing
▫ Containerless Processing

COMPETITIVE GROWTH KINETICS AND MICROSTRUCTURAL TRANSITION

ROD EUTECTIC----LAMELLAR EUTECTIC





MODEL:

V IS CONTROLLED BY UNDERCOOLING IN ROD EUTECTIC AND BY EXTERNAL COOLING IN LAMELLAR EUTECTIC

AT TRANSITION: Vrod = Vext

MEASUREMENT:

$\lambda_R = f(\Delta T)$ [Droplet, DTA]

$\lambda_R = f(V_R)$ [D.S.]

$$V_{ext} = \frac{b\,h\,\Delta T_\infty}{\Delta H_f}$$

$$\Delta T_\infty = T_{drop} - T_{gas}$$

$$\Delta H_f = 1252 \text{ joules/cm}^3$$

$$h = \frac{2K_{gas}}{d} + 0.6\left(\sqrt{\frac{u}{d}}\right) c \approx \frac{2k_{gas}}{d}$$

$\frac{vd}{\alpha_2} << 1$ for uniform T

$$K_{He} = 2 \,.\, 10^{-3} \text{ j/ s.cm.K}$$

$$B_i = \frac{hd}{K} \approx 1.3 \,.\, 10^{-2}$$

$$V_{ext} = 1.9 \cdot 10^{-5} \frac{\Delta T_\infty}{d}$$

$$V_R = 8.8 \cdot 10^{-8} \Delta T^{3.3}$$

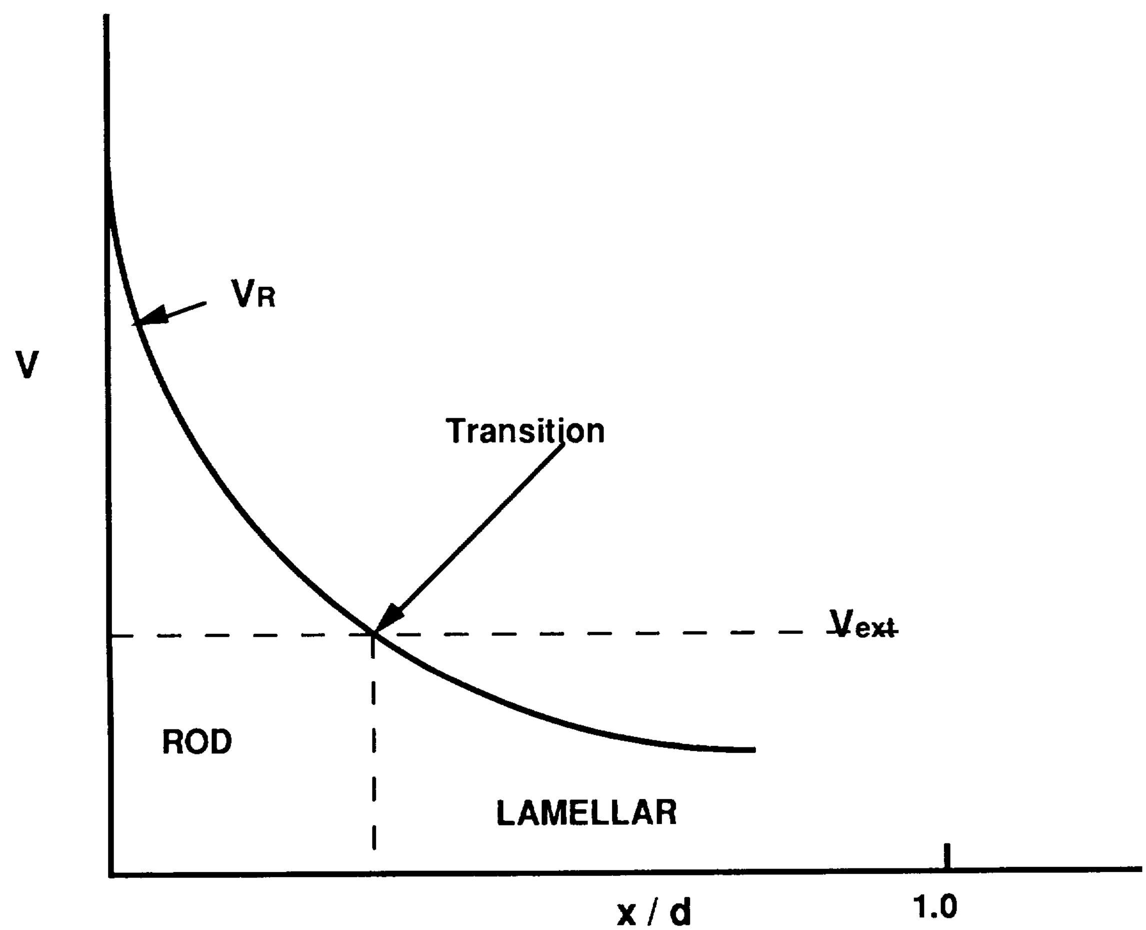
for a 36μ droplet

λ_{onset} = 960A , V_{onset} = 2.1 cm/sec

$\lambda_{transition}$ = 1100 Å

V_{ext} = 1.66 cm/sec ; V_R = 1.58 cm/sec

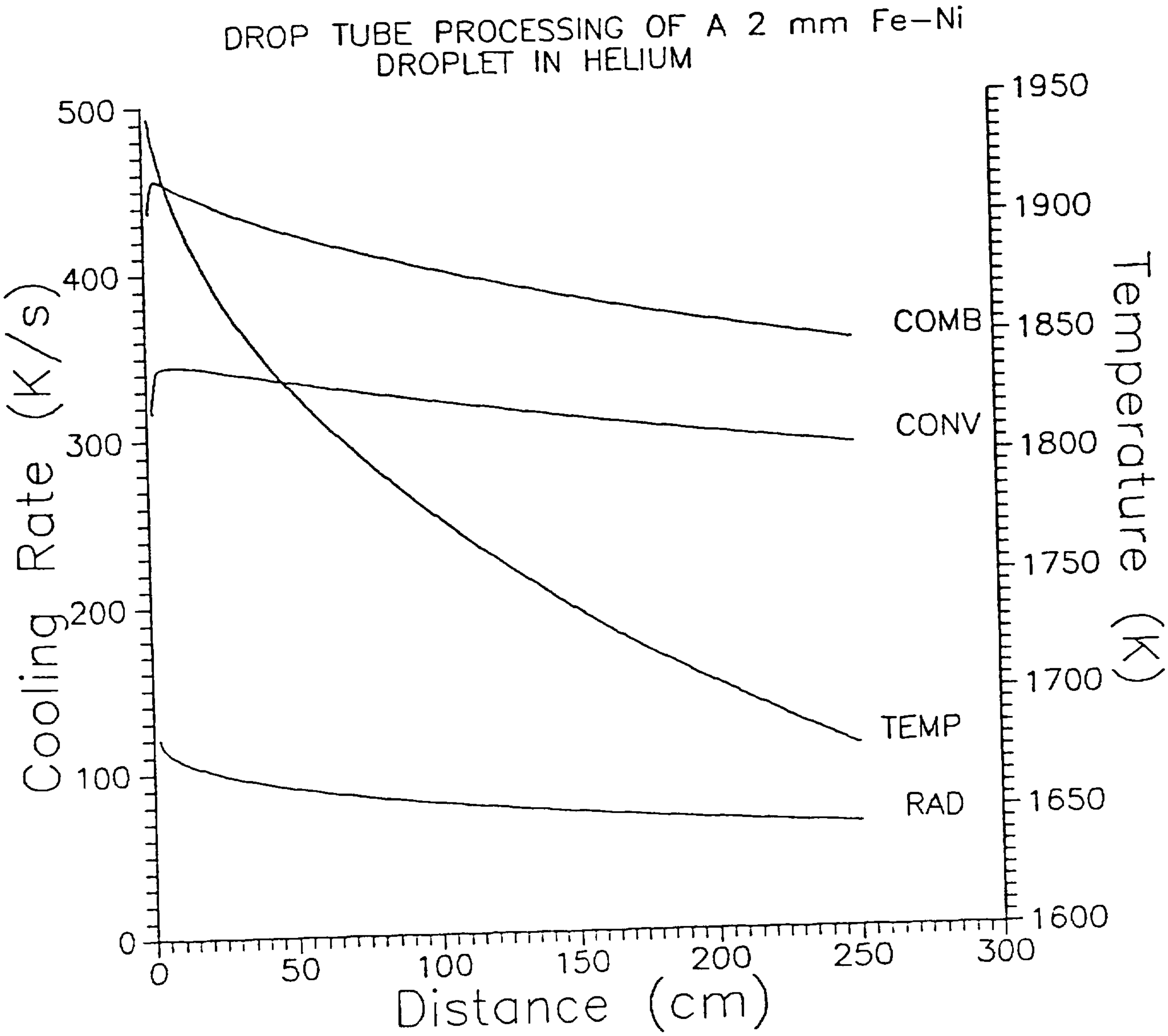
$\therefore V_{ext} \approx V_R$



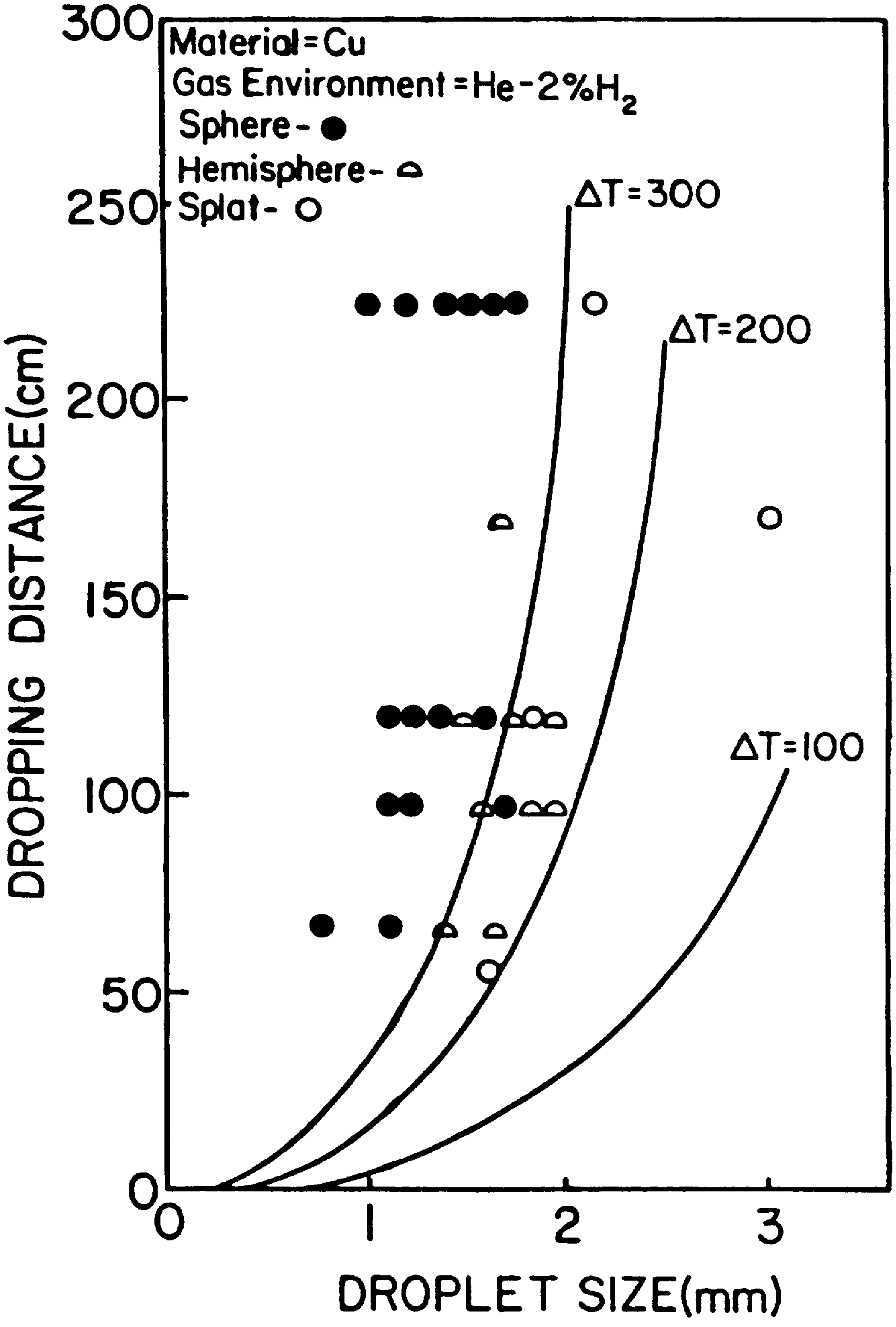
$$\frac{dT}{dt} = - \frac{\varepsilon \ A \ \sigma}{m \ c} (T^4 - T_w{}^4) - \frac{h \ A}{m \ c} (T - T_a)$$

T_a - gas film temperature $(T + T_g)/2$
T_g - gas temperature
T_w - room temperature
ε - emissivity of liquid metal
A - surface area of droplet
σ - Stefan-Boltzmann constant
c - specific heat
m - mass
h - heat transfer coefficient
t - time

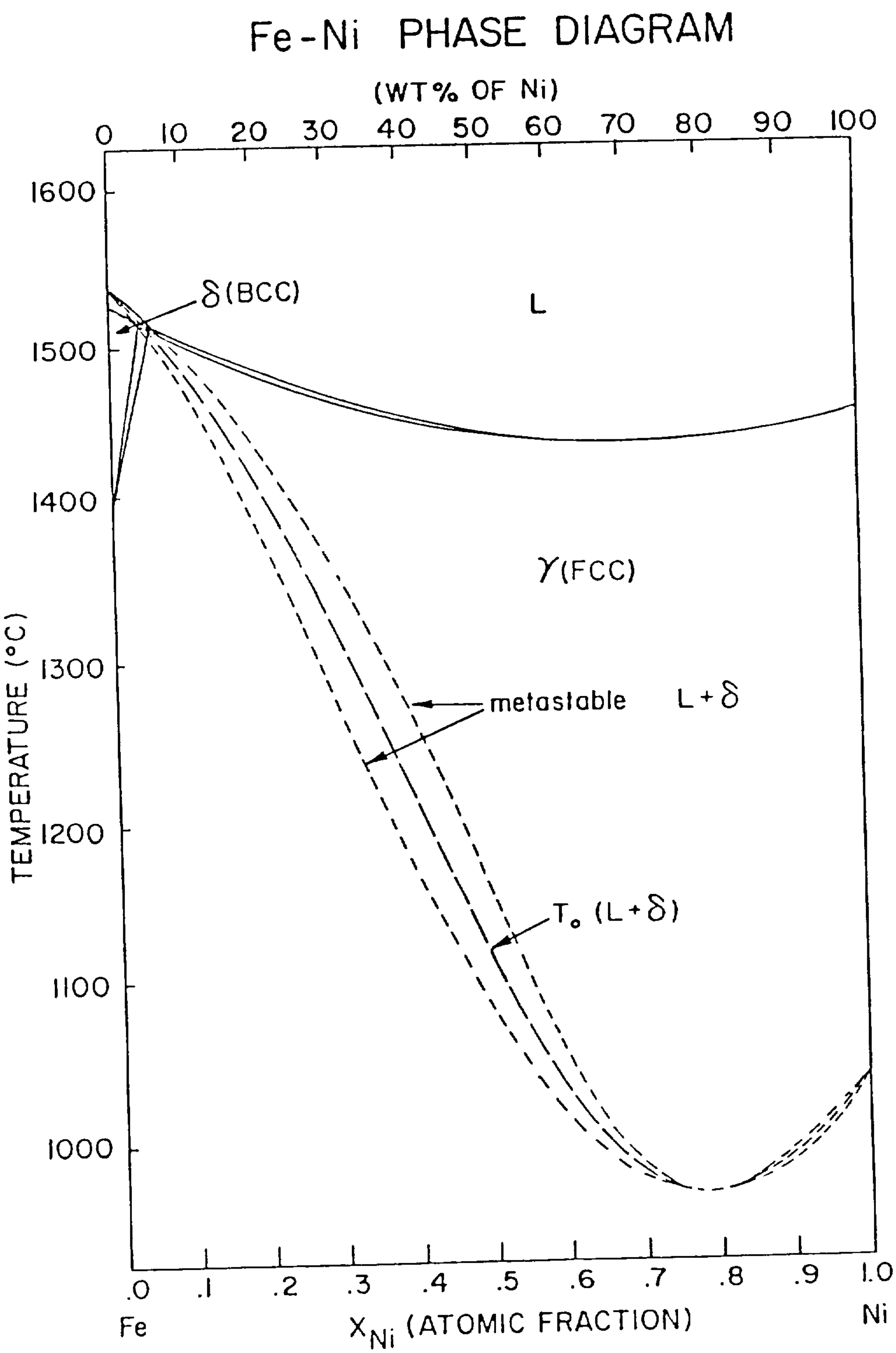
t = f(veloctiy)
v = f(distance, drag forces)



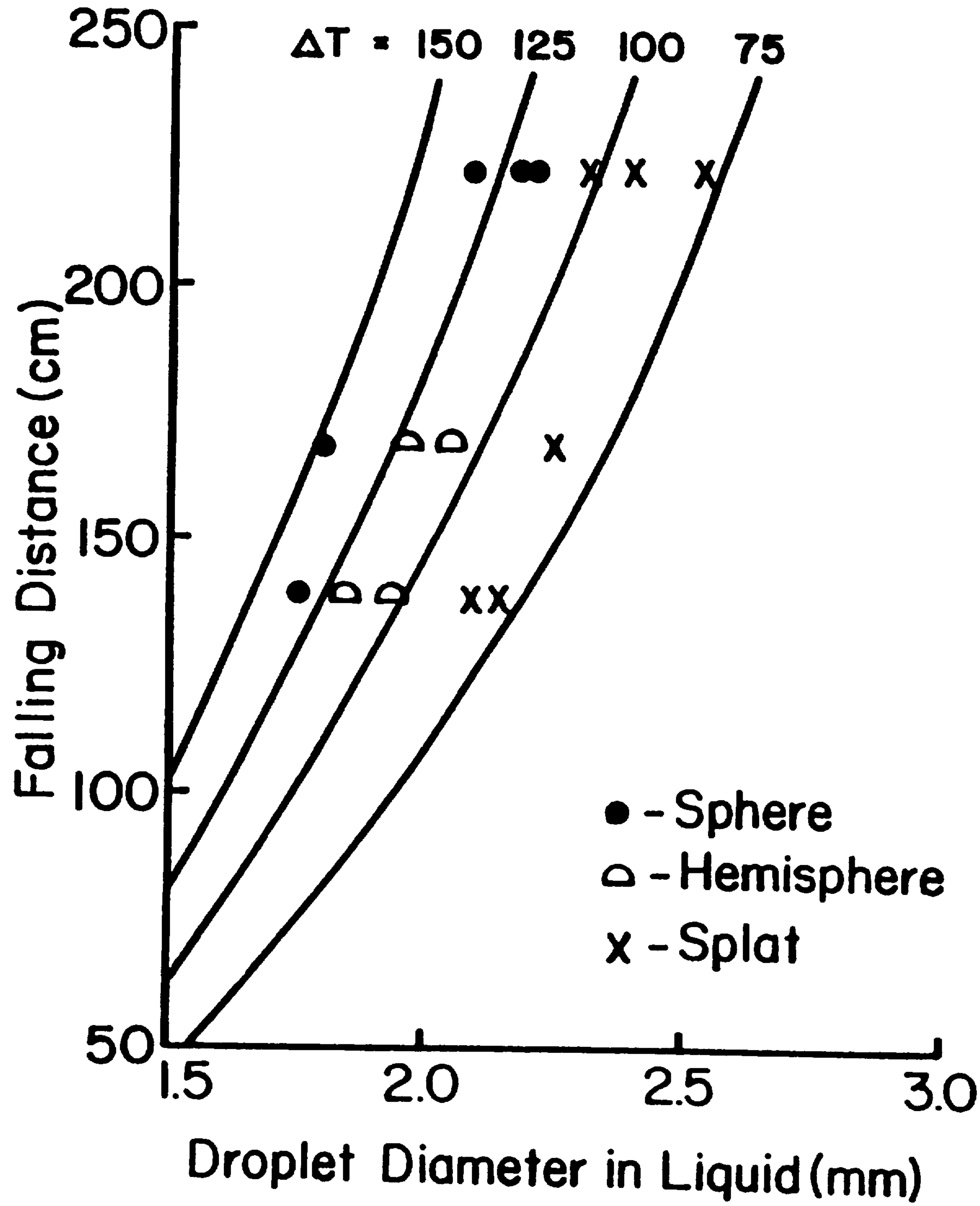
DROP TUBE PROCESSING OF A 2 mm Fe—Ni
DROPLET IN HELIUM
Cooling Rate (K/s)
Temperature (K)
Distance (cm)
COMB
CONV
TEMP
RAD
0
100
200
300
400
500
1600
1650
1700
1750
1800
1850
1900
1950
0
50
100
150
200
250
300

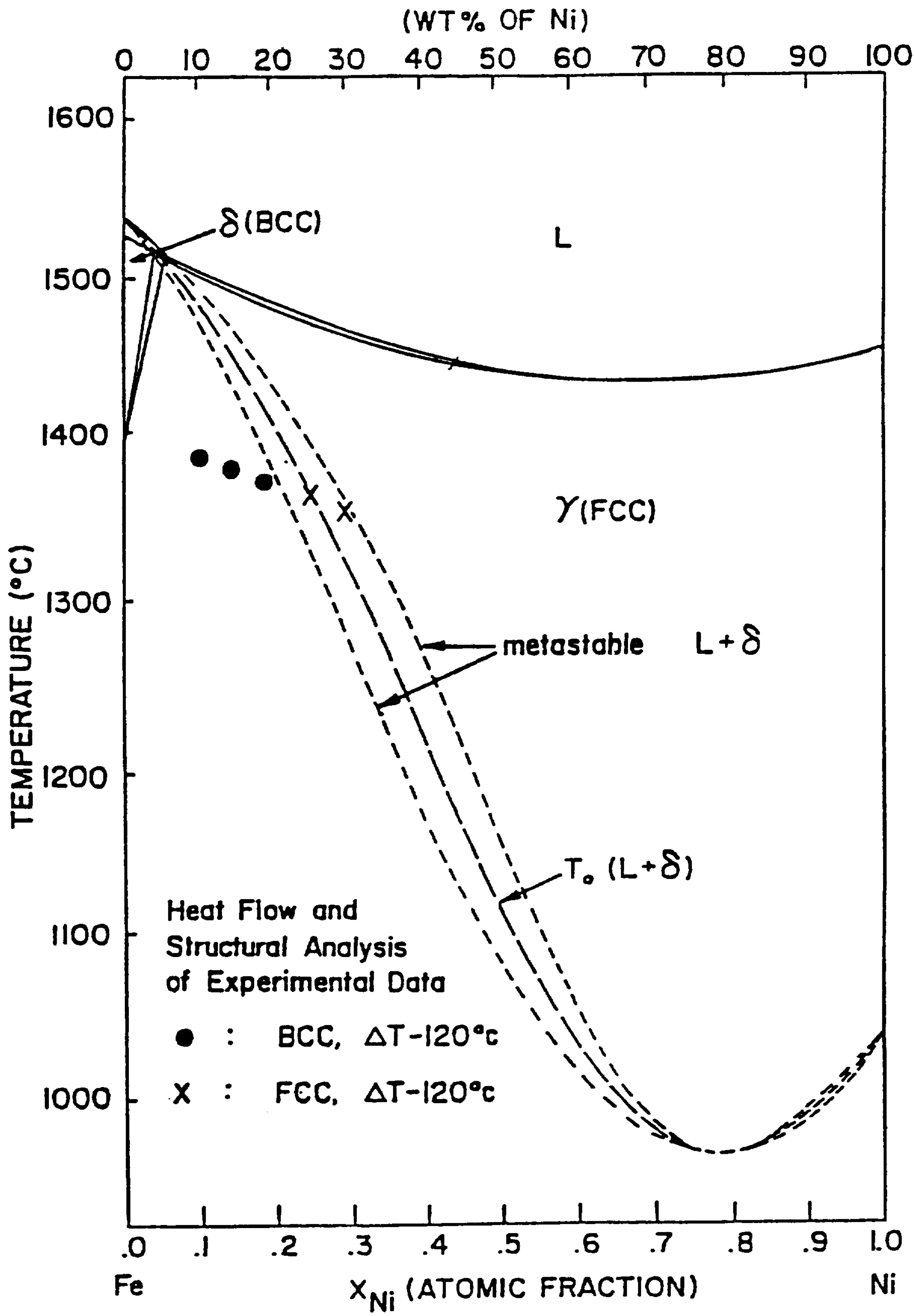


Material=Cu
Gas Environment=He-2%H_2
Sphere-
Hemisphere-
Splat-
ΔT=300
ΔT=200
ΔT=100
DROPPING DISTANCE(cm)
DROPLET SIZE(mm)
0
50
100
150
200
250
300
0
1
2
3



Fe-Ni PHASE DIAGRAM
(WT% OF Ni)
0
10
20
30
40
50
60
70
80
90
100
1600
1500
1400
1300
1200
1100
1000
TEMPERATURE (°C)
δ(BCC)
L
γ(FCC)
metastable
L+δ
T₀ (L+δ)
.0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
Fe
X_{Ni} (ATOMIC FRACTION)
Ni


ΔT = 150 125 100 75
250
200
150
100
50
Falling Distance (cm)
1.5
2.0
2.5
3.0
Droplet Diameter in Liquid (mm)
● - Sphere
◒ - Hemisphere
x - Splat


(WT% OF Ni)
0
10
20
30
40
50
60
70
80
90
100
1600
1500
1400
1300
1200
1100
1000
TEMPERATURE (°C)
δ (BCC)
L
γ (FCC)
metastable
L + δ
T_o (L+δ)
Heat Flow and
Structural Analysis
of Experimental Data
● : BCC, ΔT-120°c
X : FCC, ΔT-120°c
.0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
Fe
X_{Ni} (ATOMIC FRACTION)
Ni

POWDER SOLIDIFICATION KINETICS

* Single Nucleation Mechanism
* Random Arrangements of Nucleation Sites
  (i.e. Poisson Distribution)

$$X = \exp(-AD^n)$$

X : Nucleant-Free Fraction

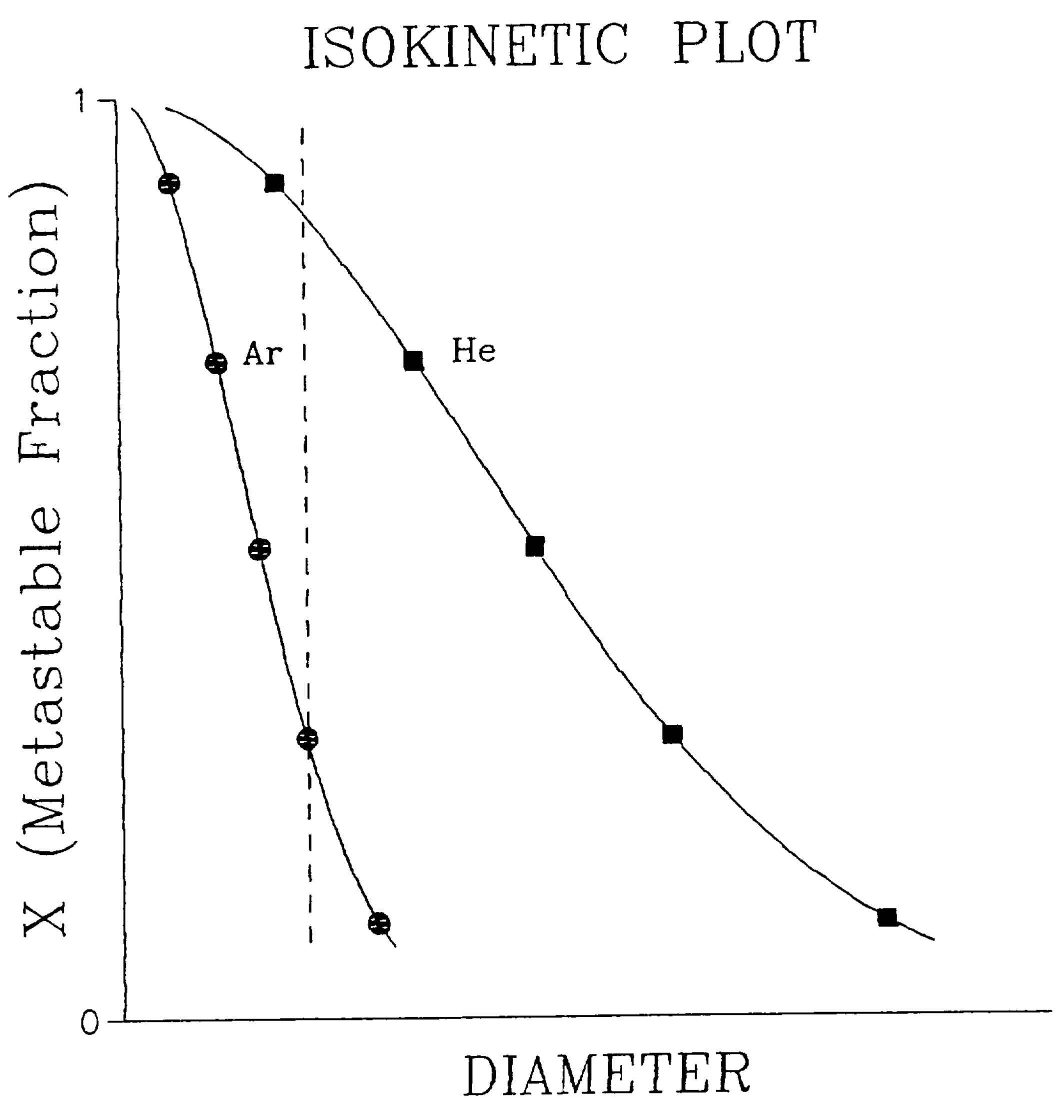
A : Constant

D : Powder Diameter

n: Related to Nucleation Mechanism

$n = 2$ Surface

$n = 3$ Volume


ISOKINETIC PLOT
1
0
X (Metastable Fraction)
Ar
He
DIAMETER

ISOKINETIC SHIFT

$$\Delta T^2 = k\ f(\dot{T})$$

Convective cooling...

$$\dot{T} = \frac{6}{\rho\ c_p\ D}\ h\ (T-T_a)$$

Low velocities and small droplet diameters...

$$\dot{T} = \frac{6}{\rho\ c_p\ D}\ \frac{2k_{gas}}{D}\ (T-T_a)$$

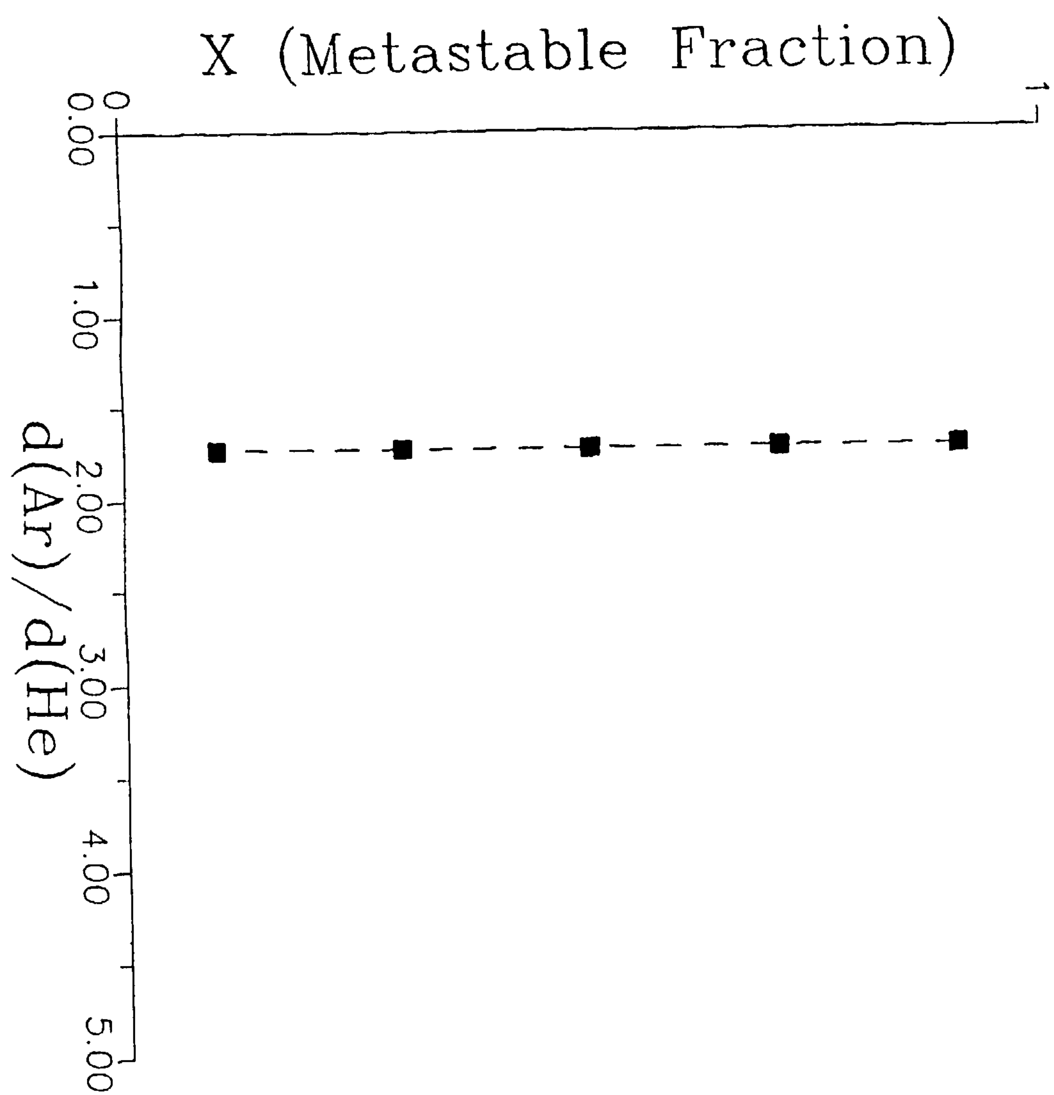
Comparing different gases...

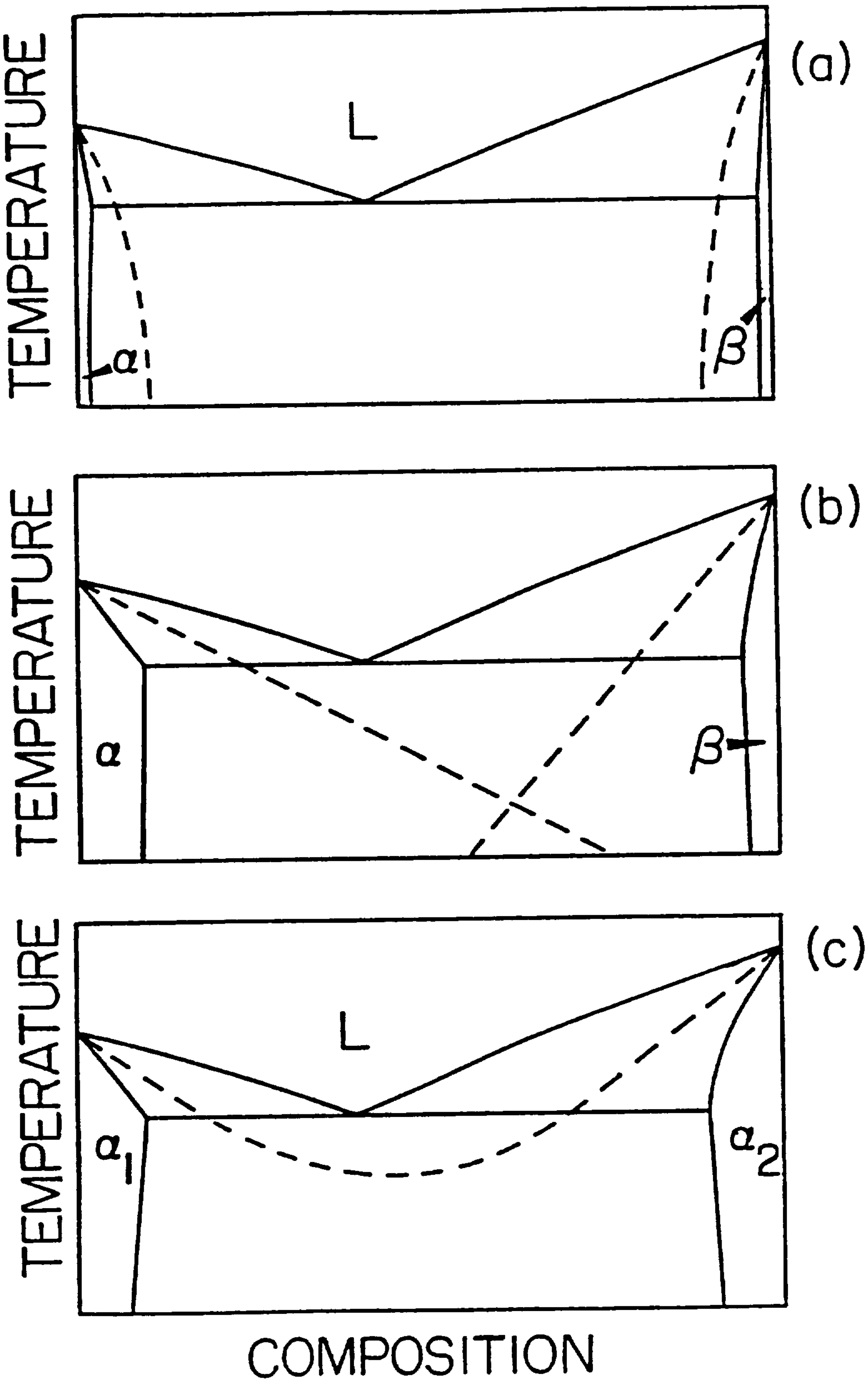
$$\frac{k_1}{k_2} = \frac{D_2{}^2}{D_1{}^2}$$

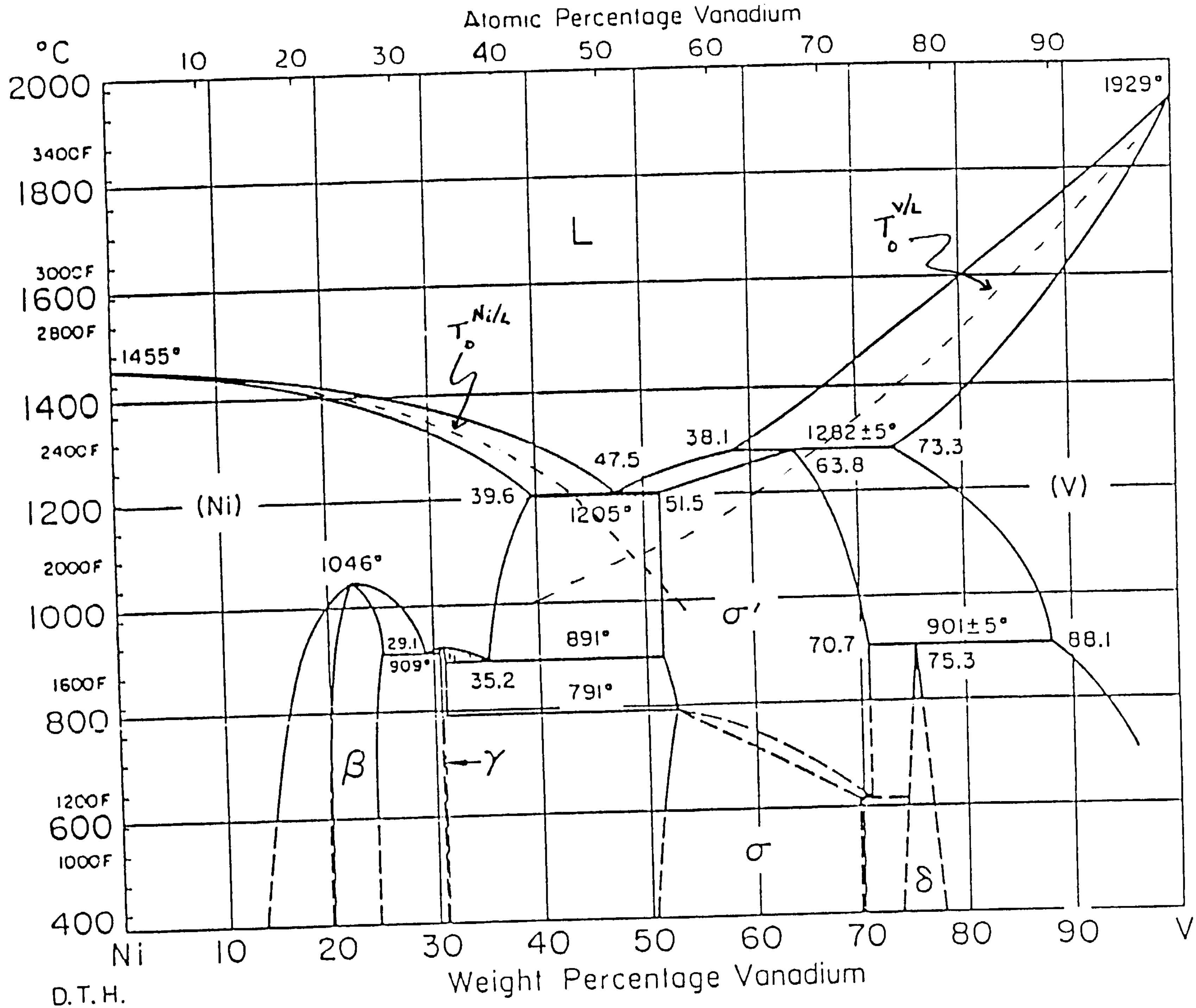
Applying to the Poisson Distribution...

$$X_{He} = \exp\left[-\left(\frac{D_{He}}{D_o}\right)^2\right]$$

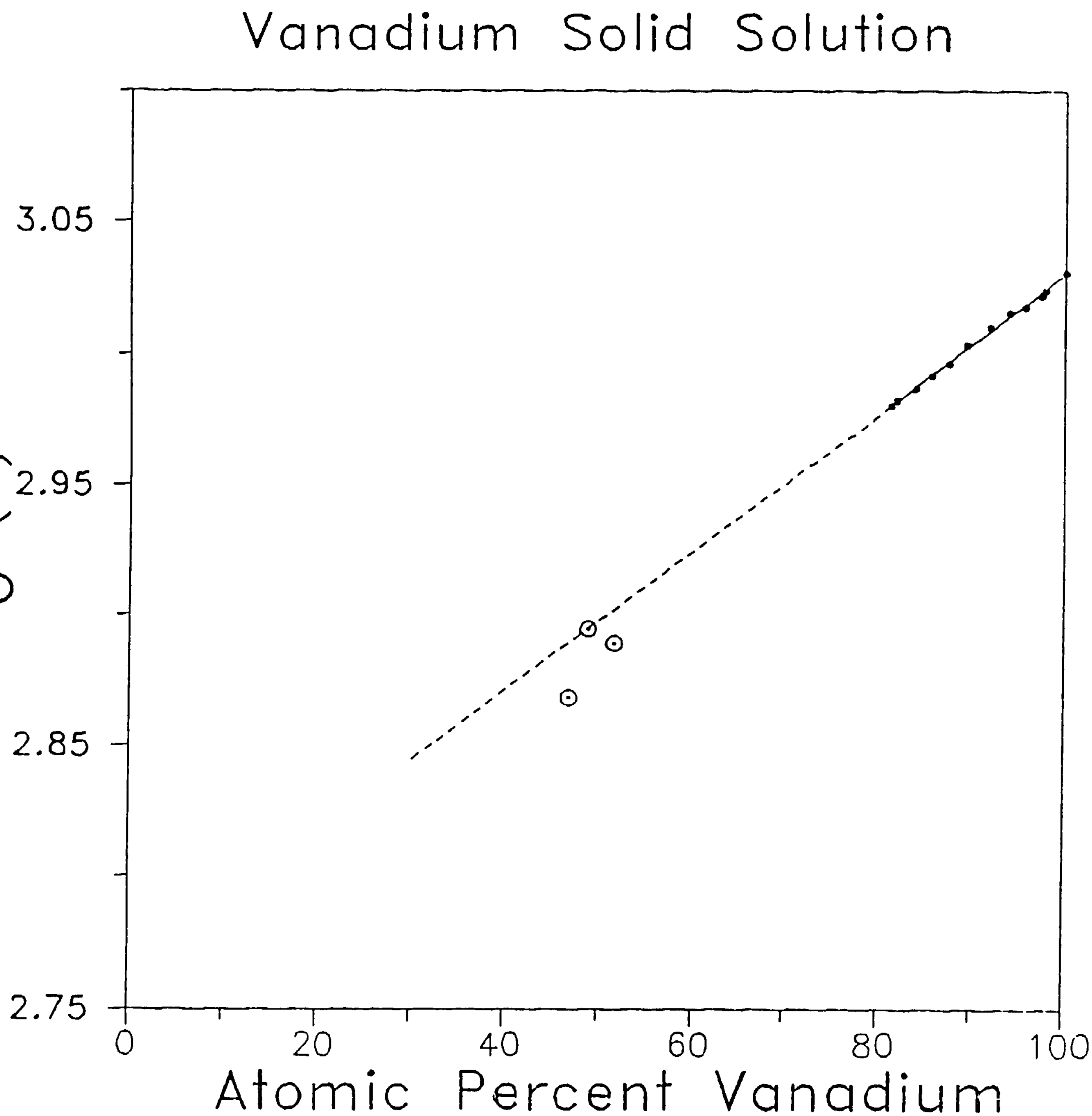
$$X_{Ar} = \exp\left[-\left(\frac{\sqrt{3}D_{He}}{D_o}\right)^2\right]$$

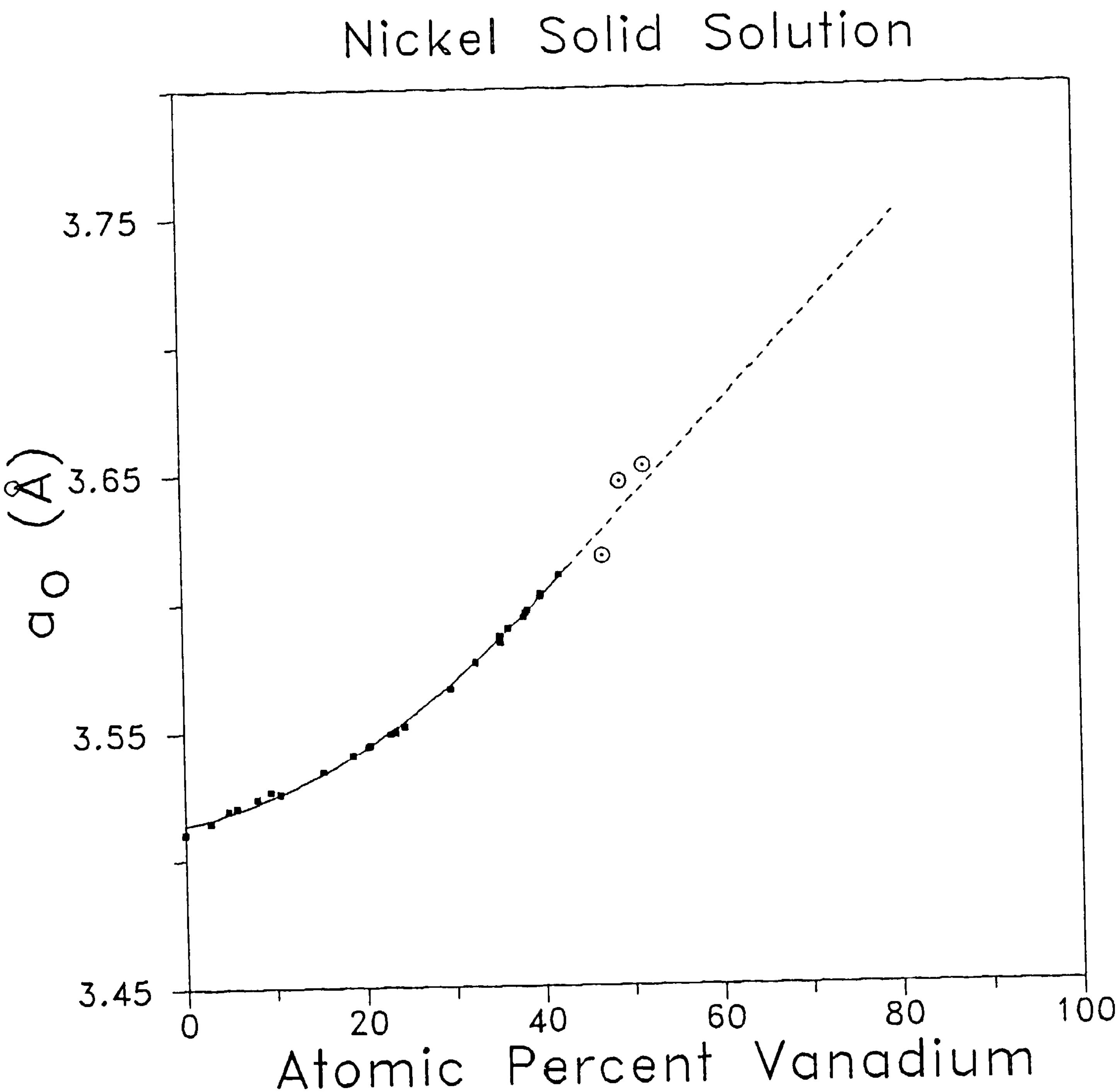

X (Metastable Fraction)
0
1
0.00
1.00
2.00
3.00
4.00
5.00
d(Ar)/d(He)


(a)
L
α
β
(b)
α
β
(c)
L
α1
α2
TEMPERATURE
TEMPERATURE
TEMPERATURE
COMPOSITION



Atomic Percentage Vanadium
°C
10
20
30
40
50
60
70
80
90
2000
3400F
1800
3000F
1600
2800F
1400
2400F
1200
2000F
1000
1600F
800
1200F
600
1000F
400
1929°
L
$T_0^{V/L}$
$T_0^{Ni/L}$
1455°
38.1
1282±5°
73.3
47.5
63.8
39.6
51.5
(V)
(Ni)
1205°
1046°
σ′
29.1
891°
901±5°
70.7
88.1
909°
35.2
75.3
791°
β
γ
σ
δ
Ni
V
Weight Percentage Vanadium
D.T.H.


Vanadium Solid Solution
3.05
2.95
2.85
2.75
0
20
40
60
80
100
Atomic Percent Vanadium
a_o (Å)



Nickel Solid Solution
3.75
3.65
3.55
3.45
a_o (Å)
0
20
40
60
80
100
Atomic Percent Vanadium

175

SUMMARY REMARKS

. Undercooled liquids expose a variety of metastable states and Microstructure options

. Containerless processing offers an important background experience to control undercooling, and to process undercooled liquids so that successful microgravity experiments can be undertaken

. Microgravity and Earth-based experiments should be coodinated

SUMMARY

- Progress in Undercooling Control and Analysis
    - Sample size scale-up
    - Surface sensitivity
- Microstructure / Kinetic Transitions
- Metastable Phase Diagrams
    - Interpret non-equilibrium effects
    - Identify microstructural options (Alloy design)
    - Can be accessed experimentally
    - Several variations possible
- Containerless Processing
    - Microstructural probe of undercooling
    - Heat flow analysis
    - Need direct non-contact temperature measurement
    - Measured kinetic response-Processing