

Microsegregation in Manganese Steels

by

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**Thesis submitted in fulfilment of the degree of
Doctor of Philosophy at the Department of Metallurgy
of the University of Sheffield**

August 1989



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**TEXT BOUND CLOSE TO
THE SPINE IN THE
ORIGINAL THESIS**

FIGURES

Figure 1

Columnar and equiaxed solidification of a pure substance (7)

Figure 2

Constitutional undercooling in alloys (7)

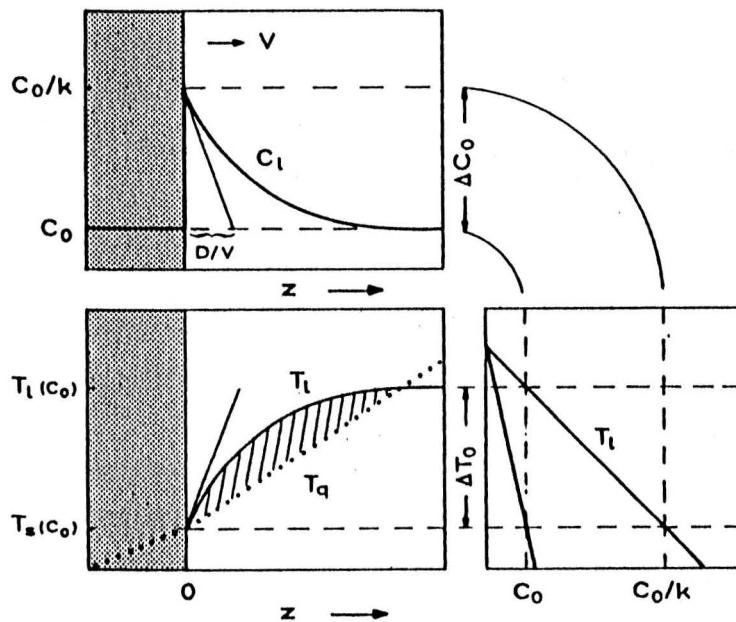
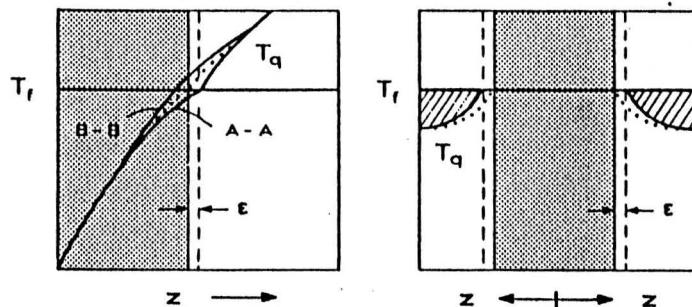
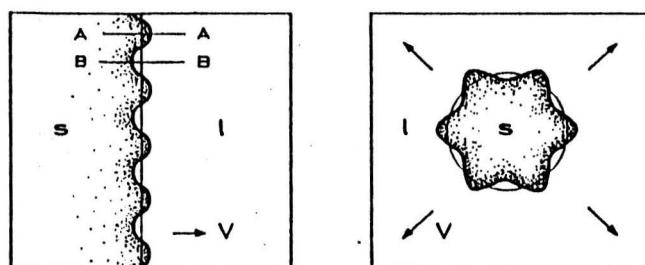
a**b**

Figure 3

Results of Nash and Glicksman for dendrite tip radius and growth velocity (solid circle), related to graphs of V and r from Ivantsov, modified Ivantsov and Temkin (18)

Figure 4

Dependence of tip radius (R) and primary arm spacing (λ_1) on the dendrite growth velocity (V). (7)

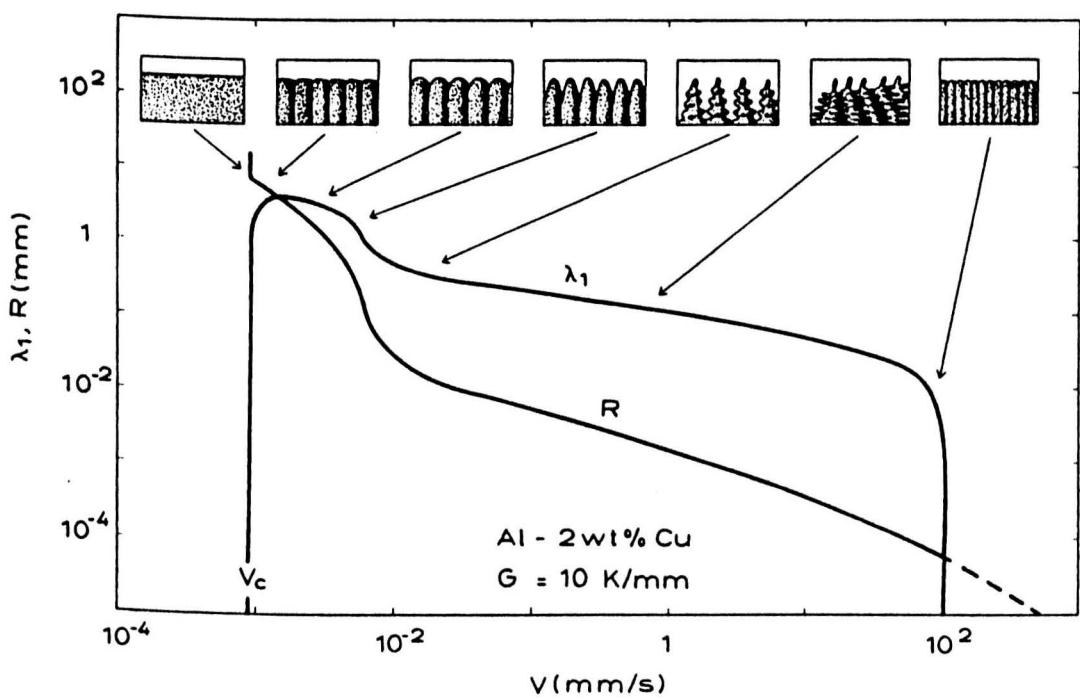
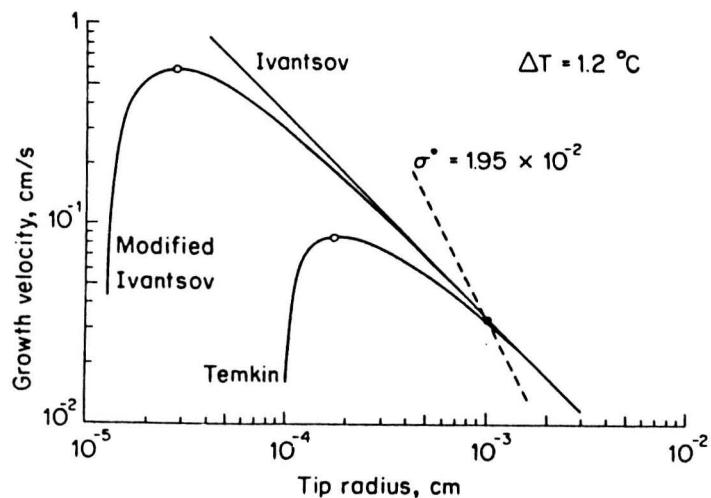


Figure 5

Comparison of the Kurz-Fisher and Hunt theories of primary spacing with the experimental data in succinonitrile- 5.5 mol pct. acetone system. Temperature gradient = 67 K/cm (30)

Figure 6

A quantitative comparison of the thermal gradient dependence of the primary arm spacings with the theoretical predictions for the directionally solidified alloys. (50)

a) Pb- 8 pct Au, V = 10 mm/sec

b) Pb- 3 pct Pd, V = 1.2 mm/sec

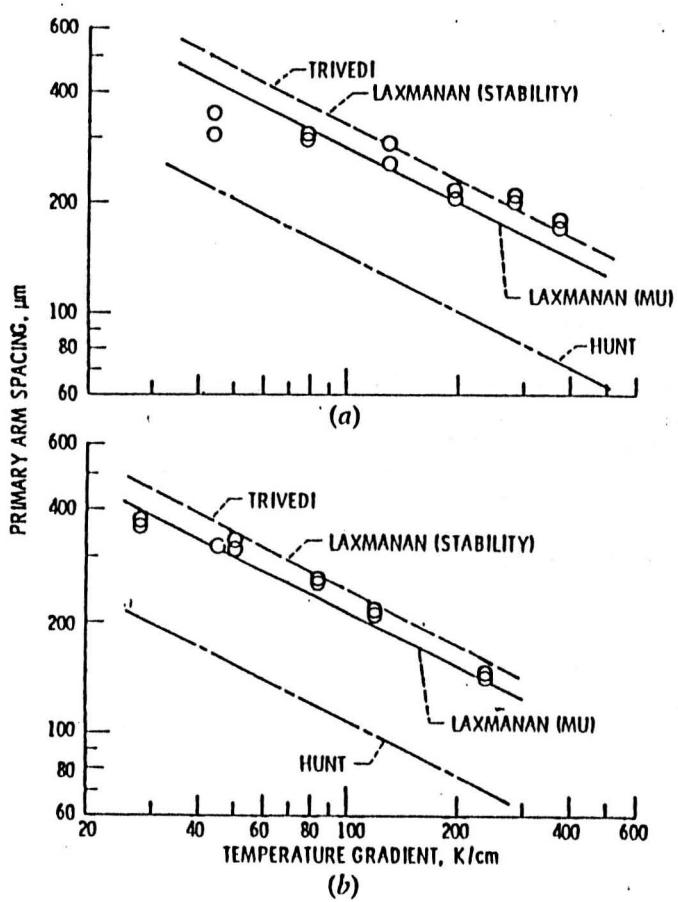
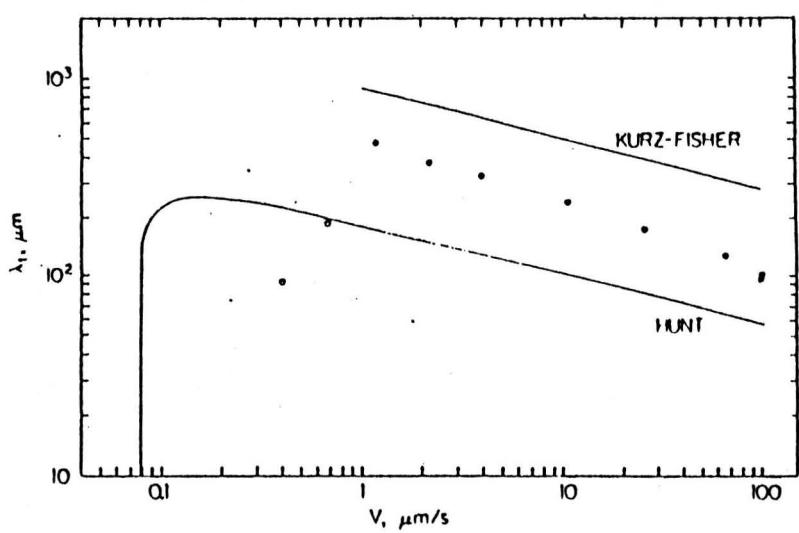


Figure 7

**Secondary dendrite arm spacings as a function of cooling rate
in commercial steels containing from 0.1 to 0.9 % C (54)**

Figure 8

Secondary dendrite arm coarsening mechanisms (ripening) (51)

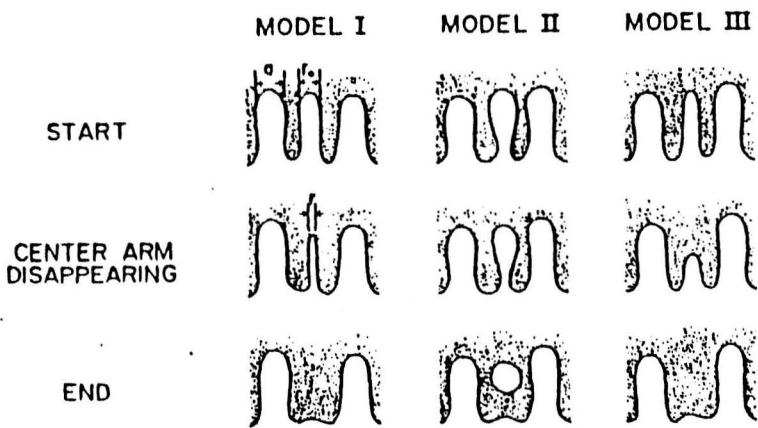
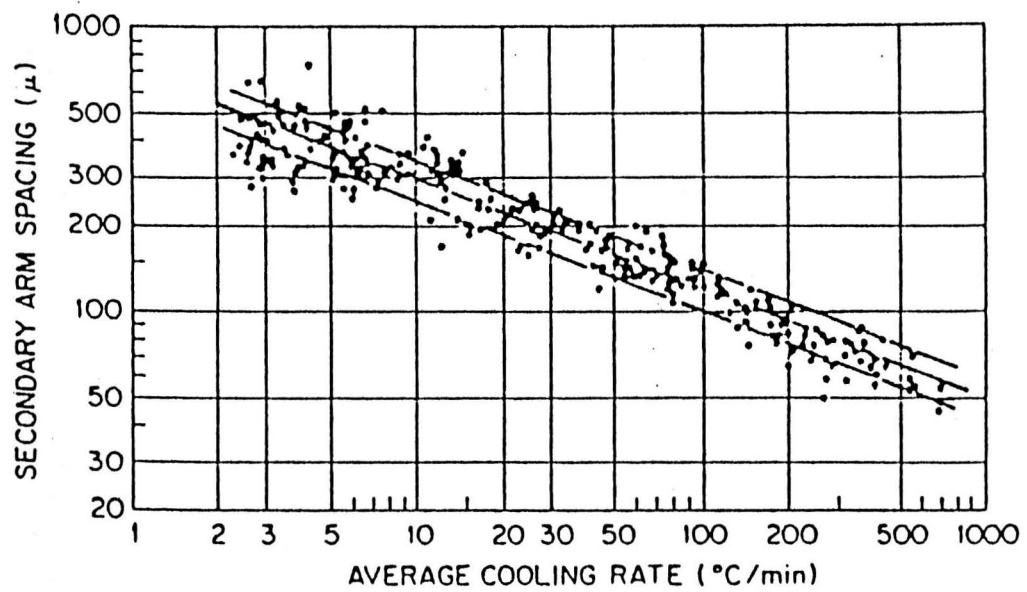


Figure 9

Schematic diagram showing the coalescence model (42)

λ_2 is the secondary dendrite arm spacing

r_A is the radius of curvature of the root of the interdendritic region

r_B is the radius of curvature of the dendrite tip

l is the length of a dendrite

Figure 10

Comparison between experimental secondary dendrite arm spacings and theoretical predictions in Al- 4.5 pct % Cu alloy as a function of time during solidification for different cooling rate.(60)

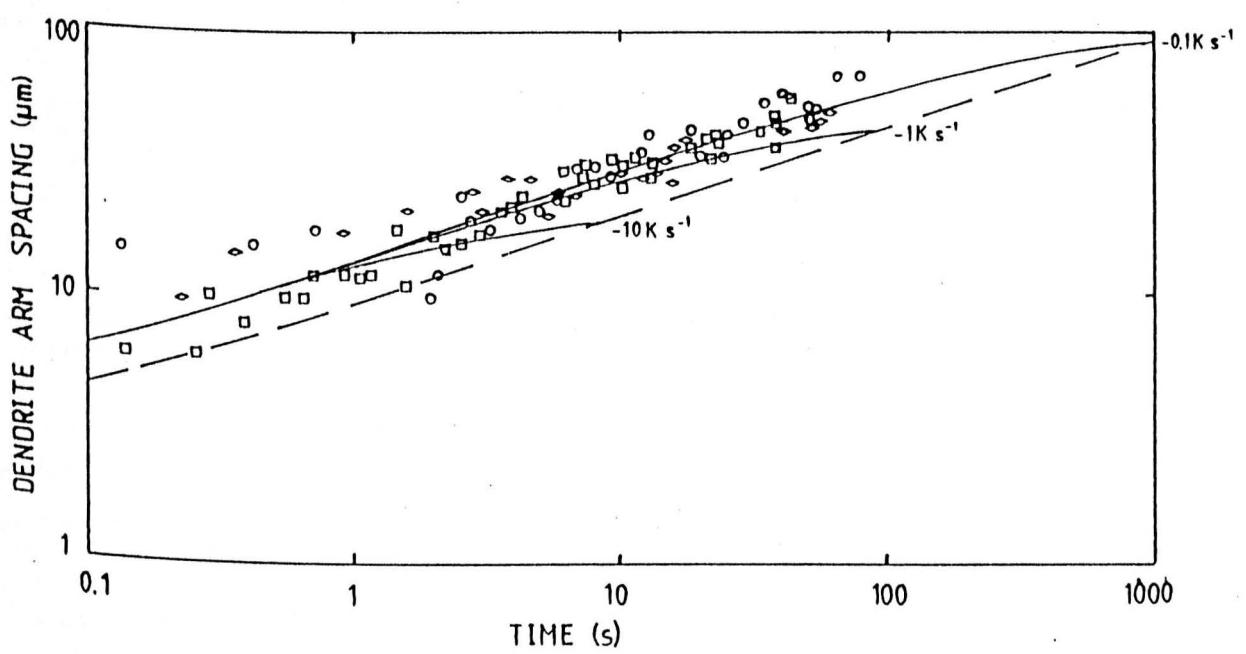
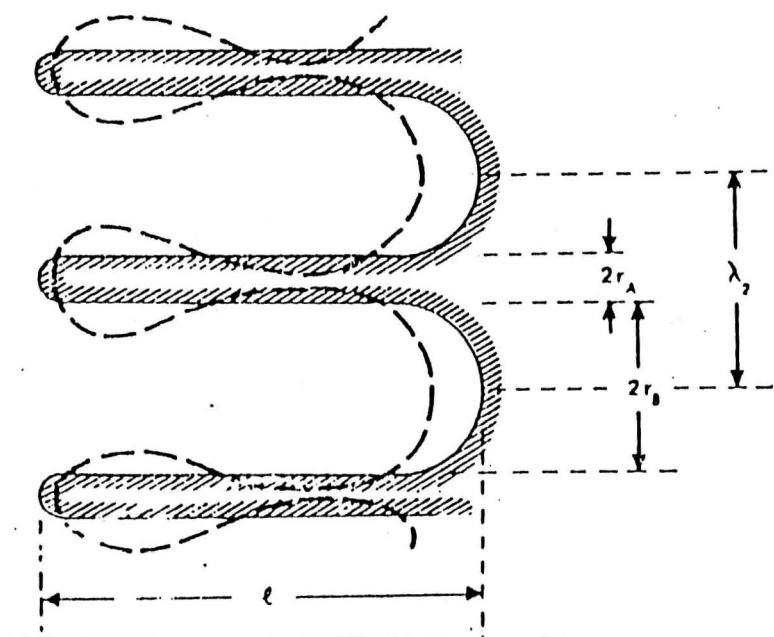


Figure 11

Mechanism of temperature gradient zone melting (TGZM) (65)

Figure 12

Model of interdendritic solidification showing solute distribution in the liquid, a , when TGZM is dominant, b , when solidification is dominant (65)

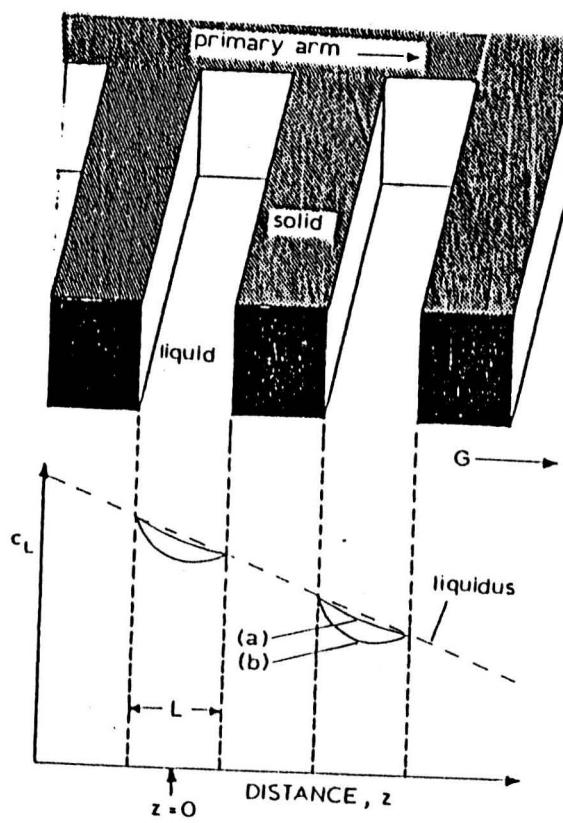
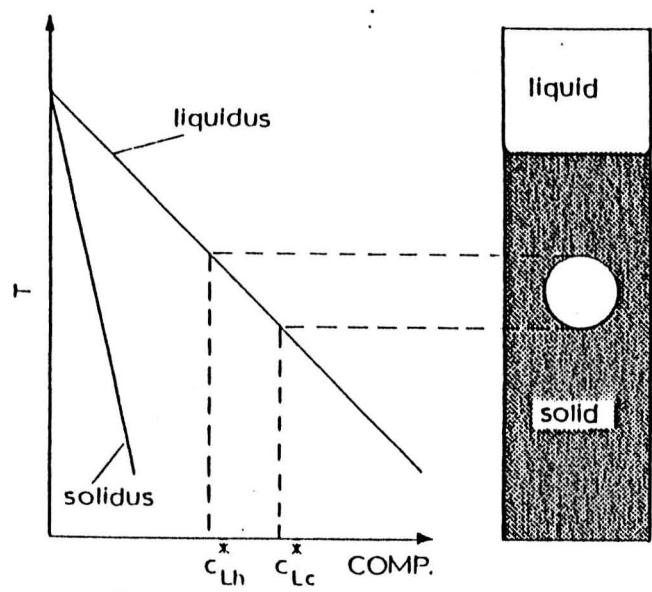
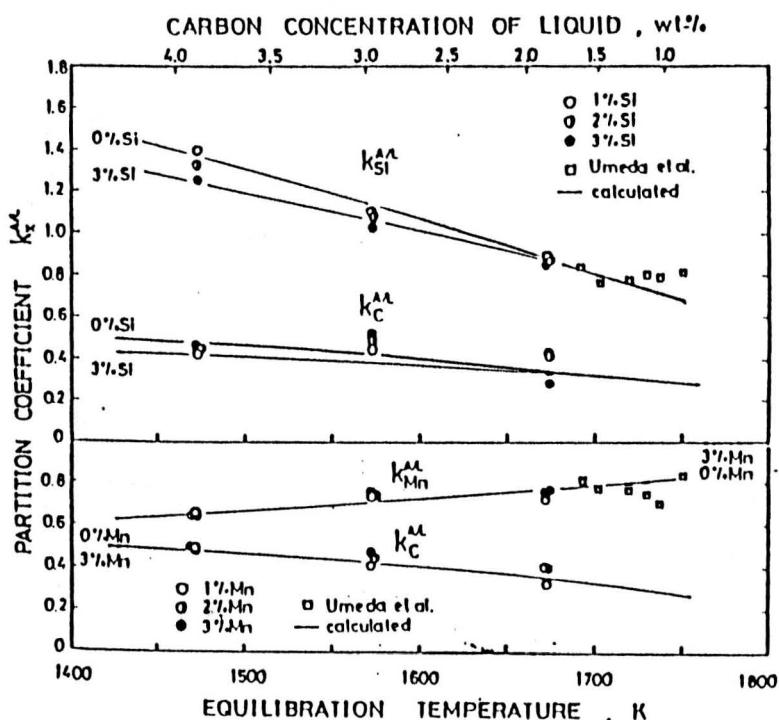
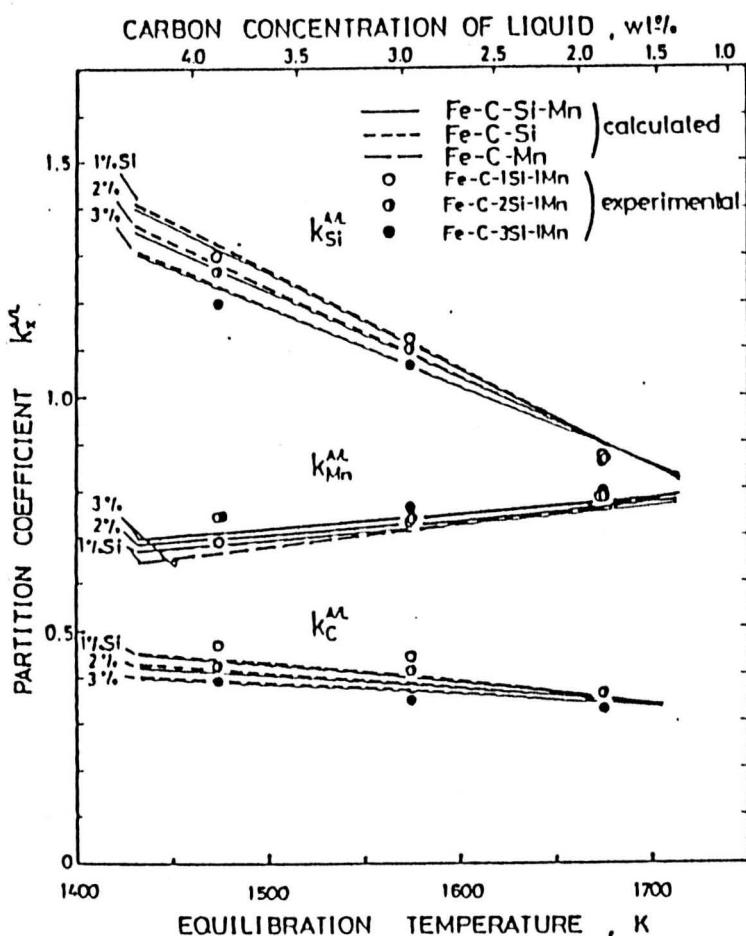


Figure 13

Coefficients of equilibrium partition of solute elements between austenite and liquid iron in Fe-C-Si and Fe-C-Mn ternary alloys(a) and in Fe-C-Si-Mn quarternary alloys(b); C concentration of liquid is for Fe-C binary system (81)



(a)



(b)

Figure 14

The iron-carbon equilibrium diagram (170)

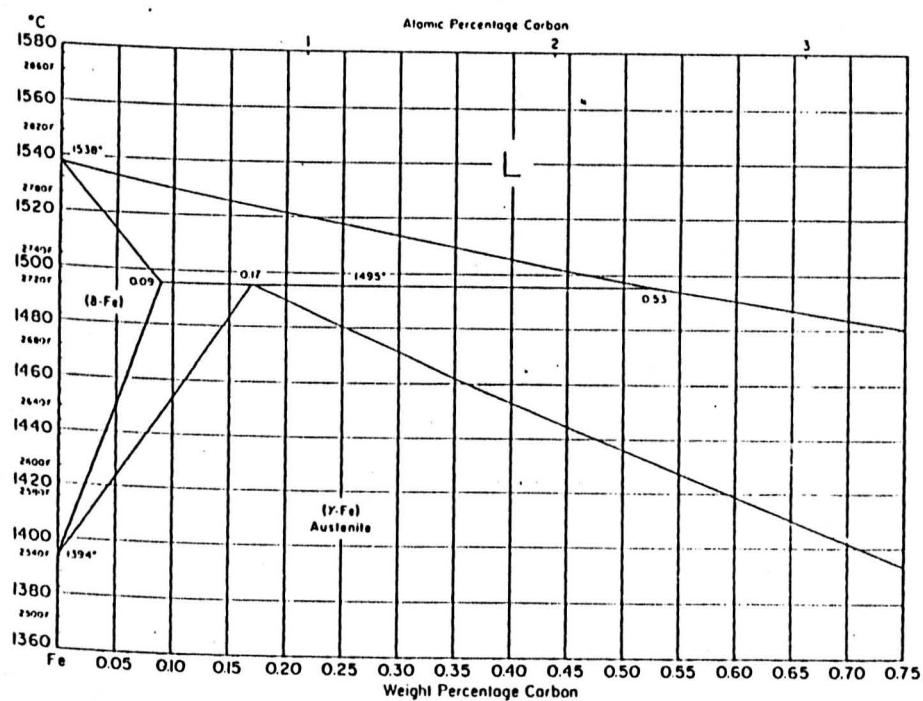
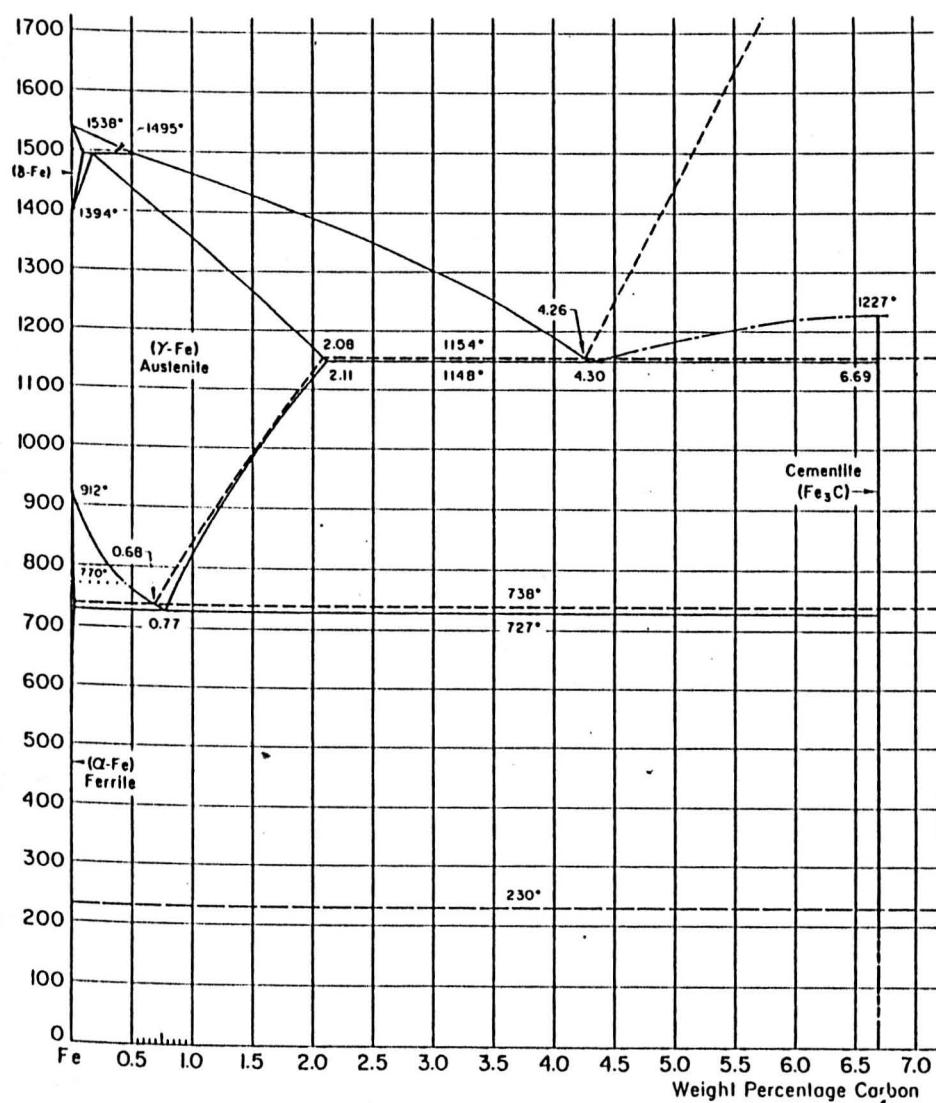


Figure 15

The iron-manganese equilibrium diagram (170)

Figure 16

The manganese-carbon equilibrium diagram (170)

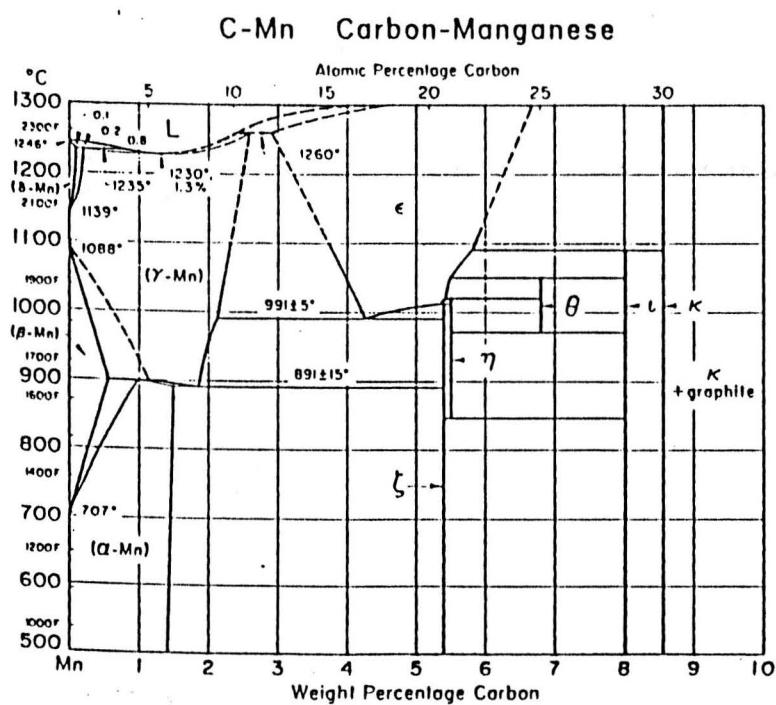
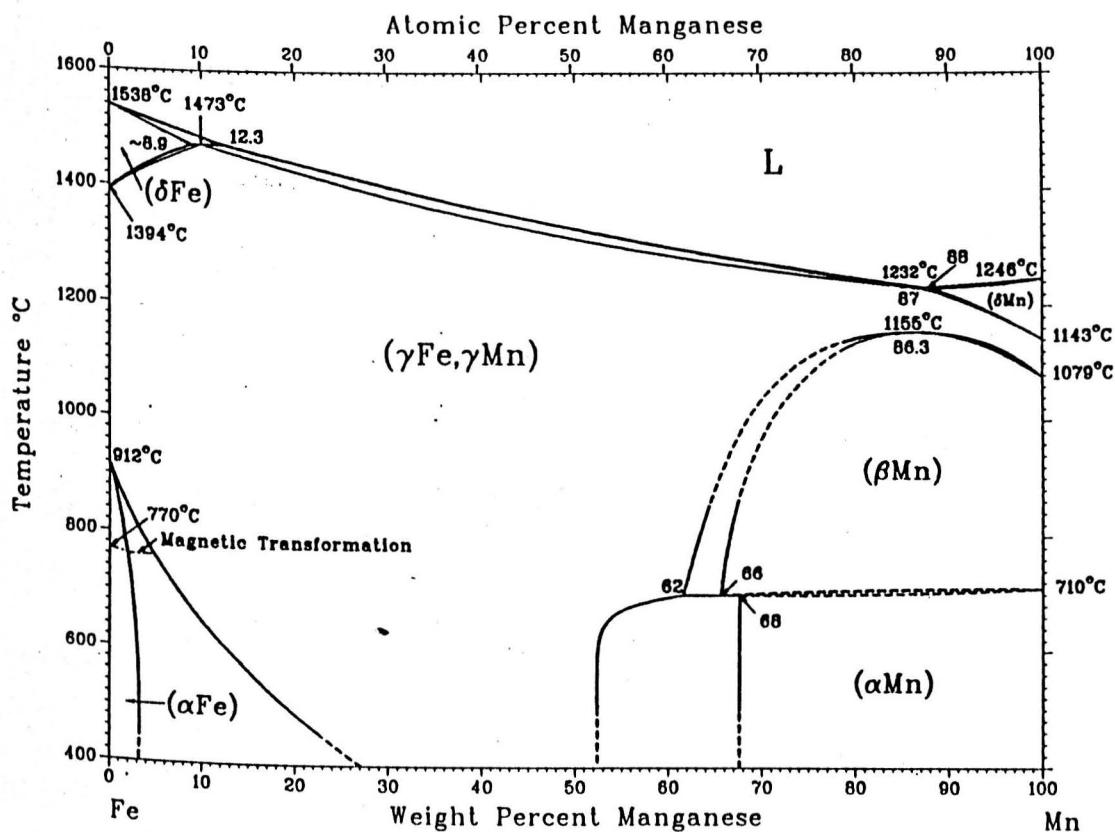


Figure 17

The peritectic corner of the Fe - C - 1.5 % Mn equilibrium diagram (132)

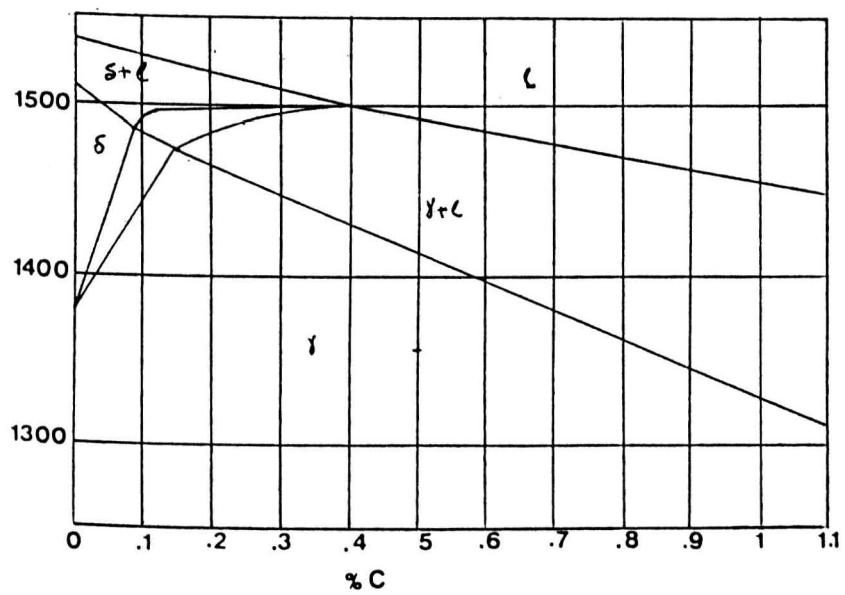


Figure 18

Photograph of directional solidification furnace

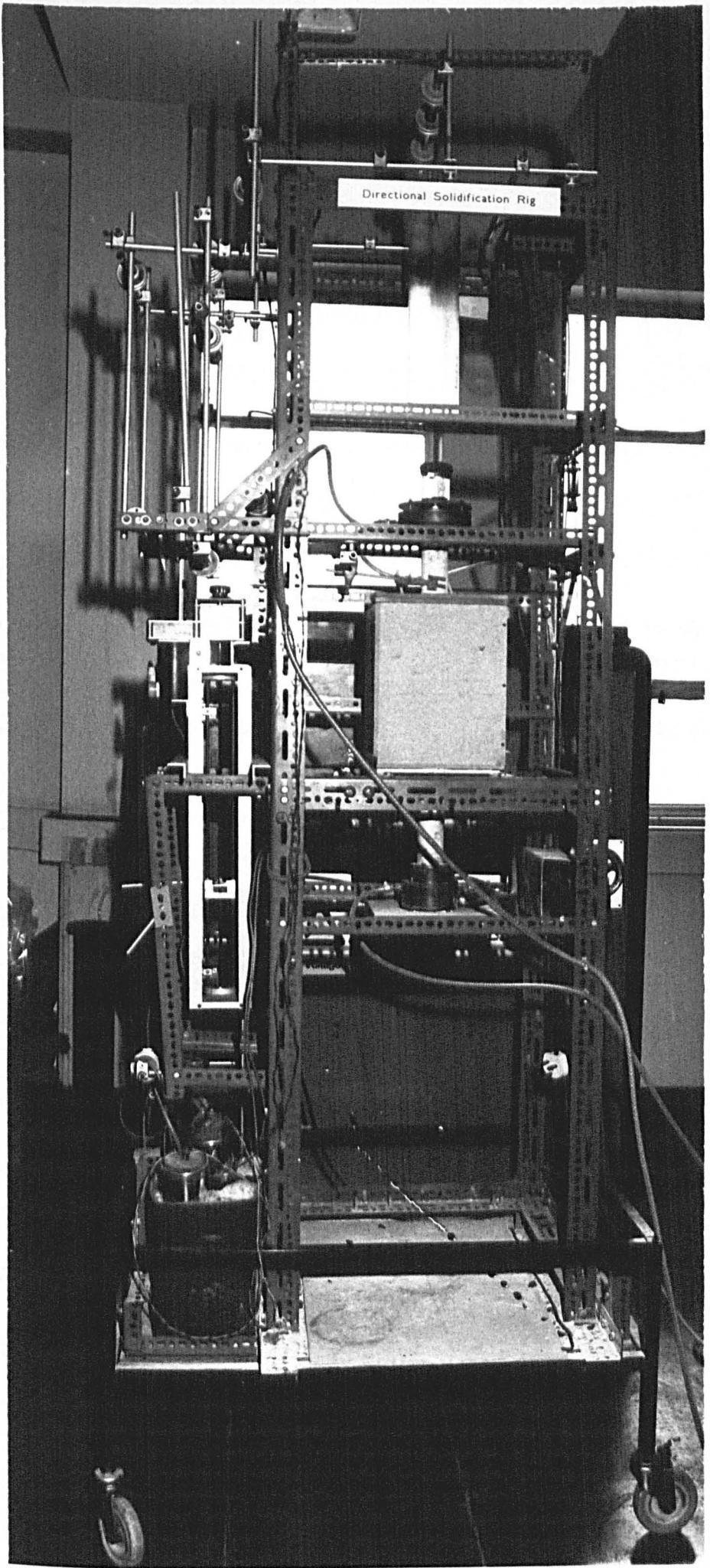


Figure 19
Schematic of directional solidification furnace

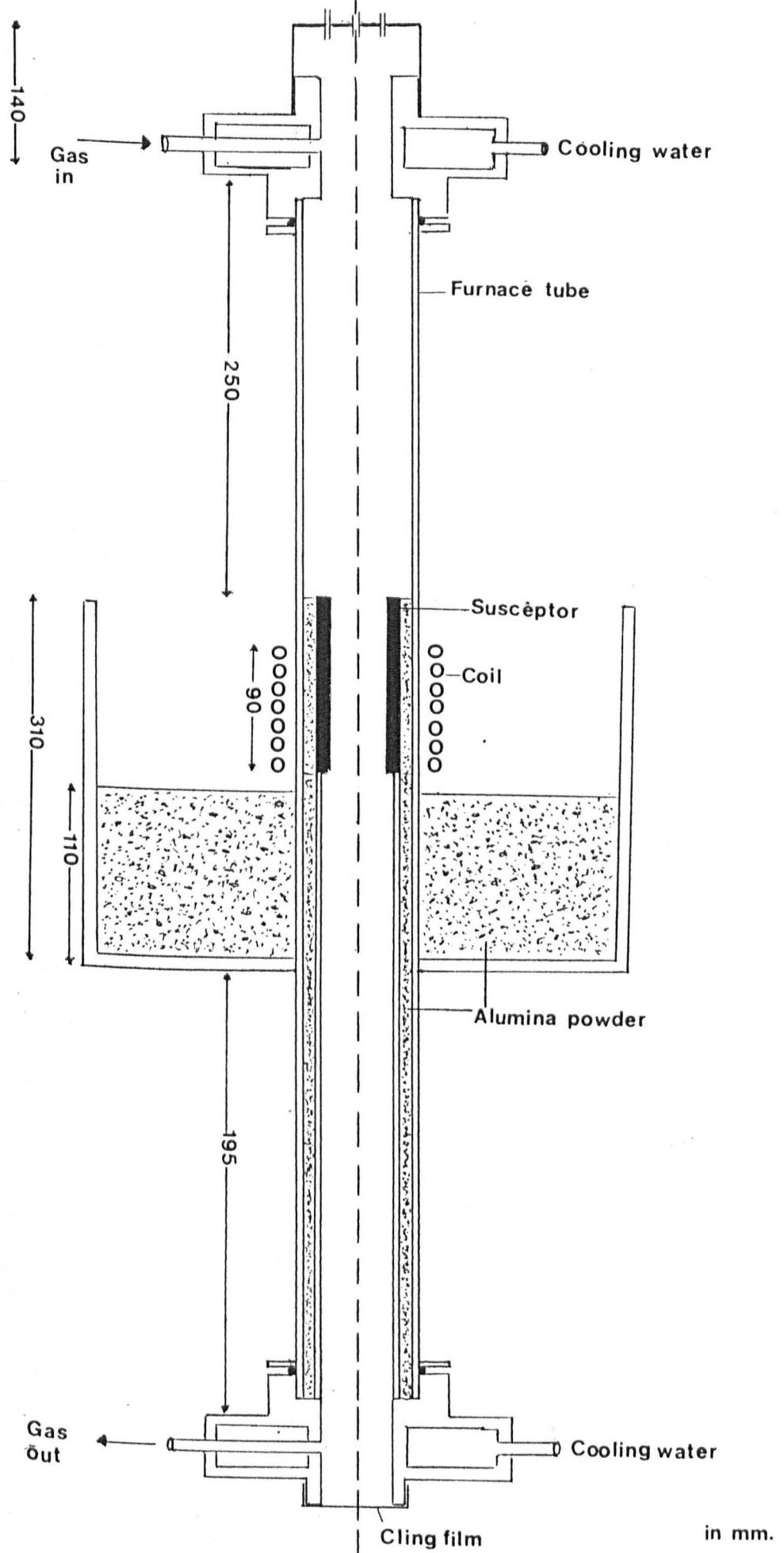


Figure 20

Construction of thermocouple and specimens

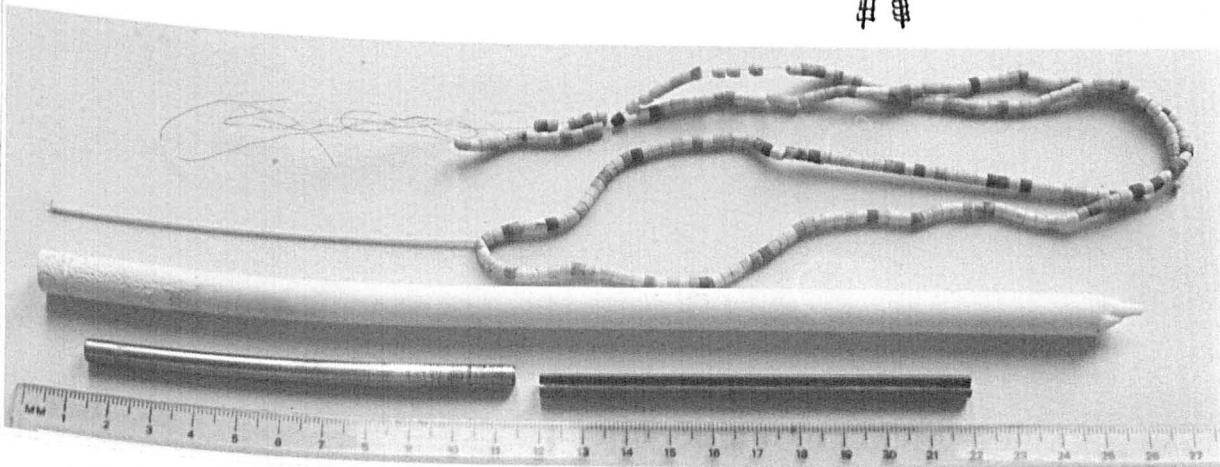
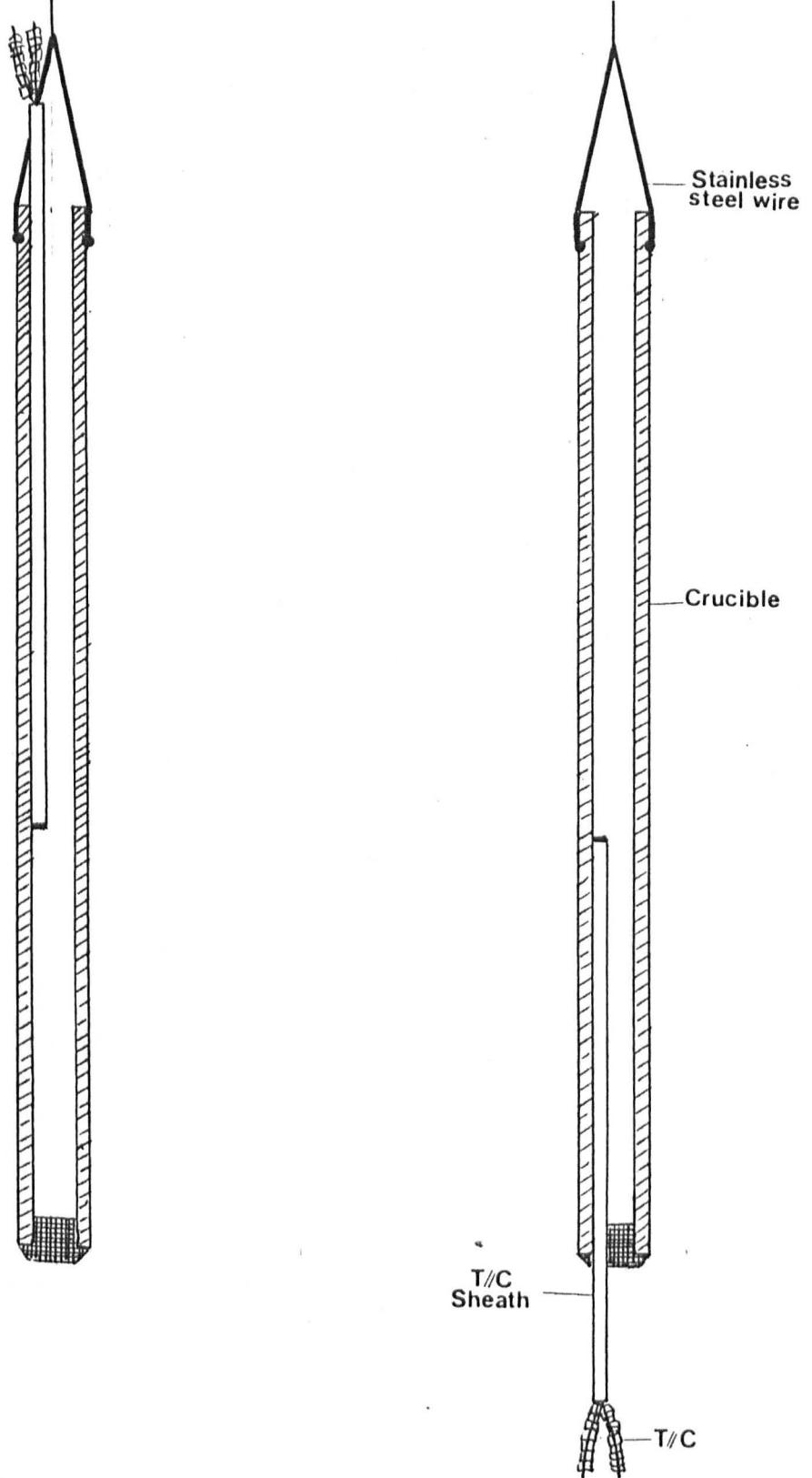


Figure 21

The cylindrical cellular primary arm model

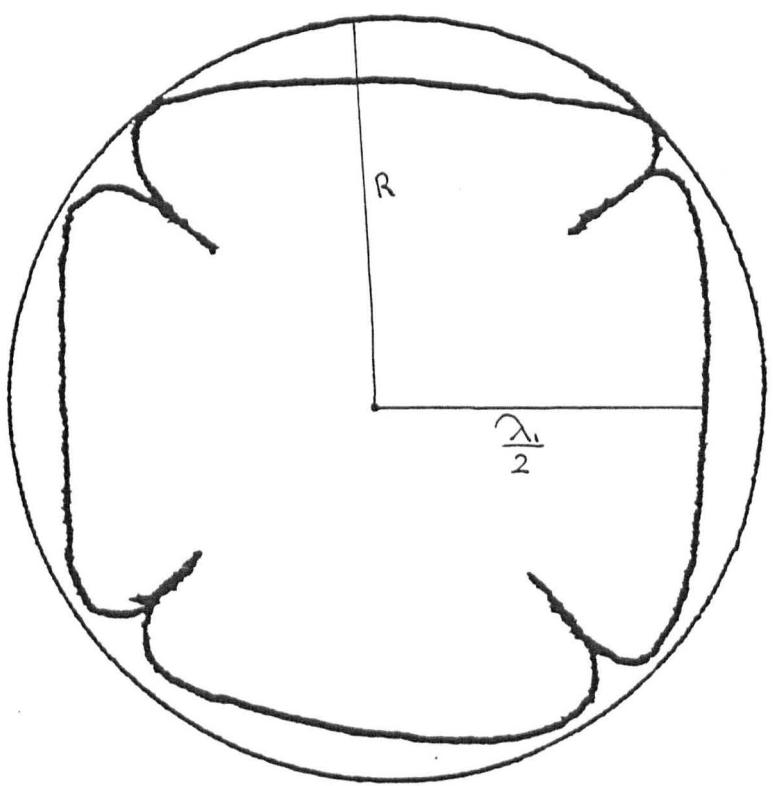


Figure 22

- a) the tranverse section of close packed primary arm spacing arrangement
- b) the two extreme possible arrangement of secondary arms on the longitudinal section showing concave solidification model

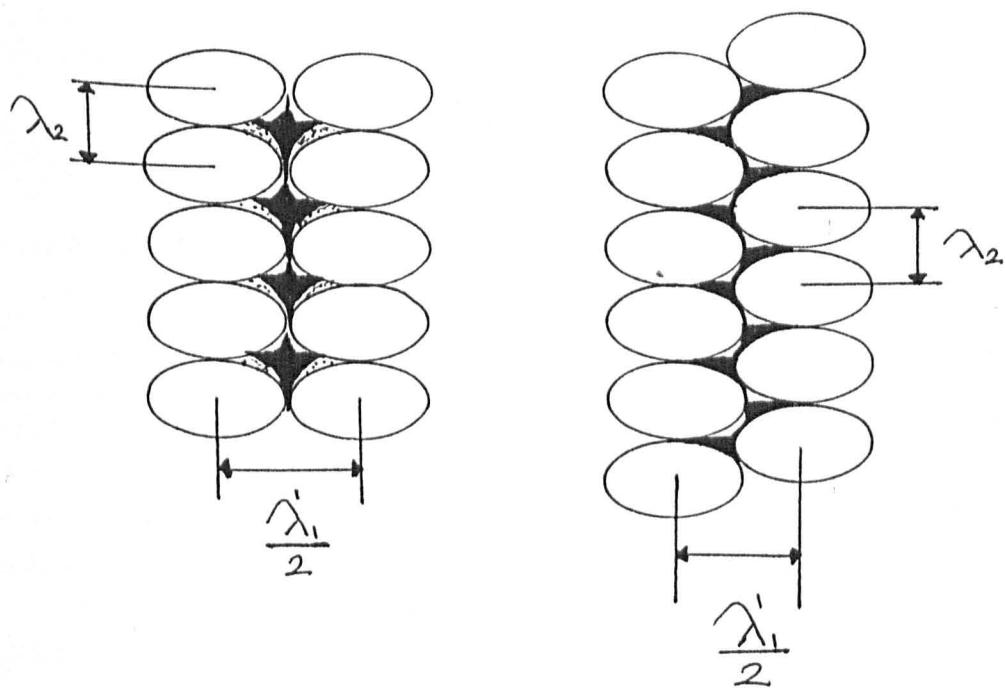
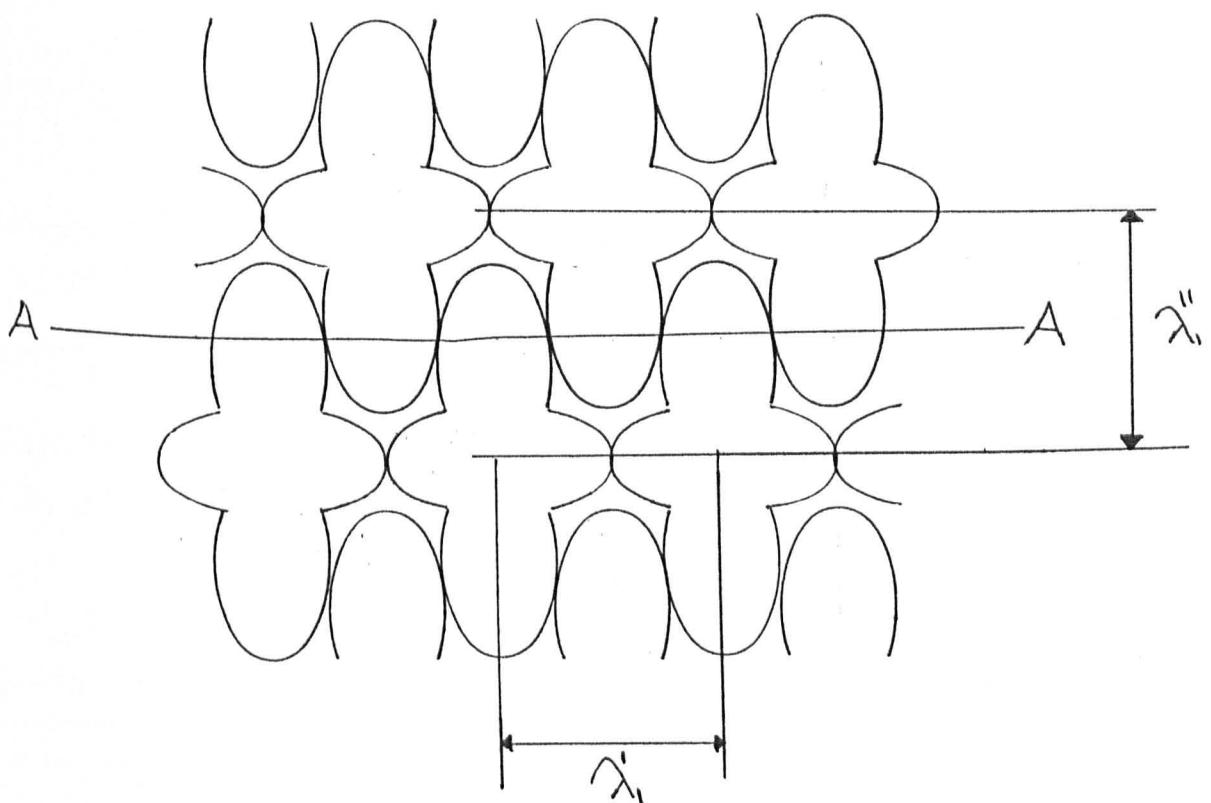
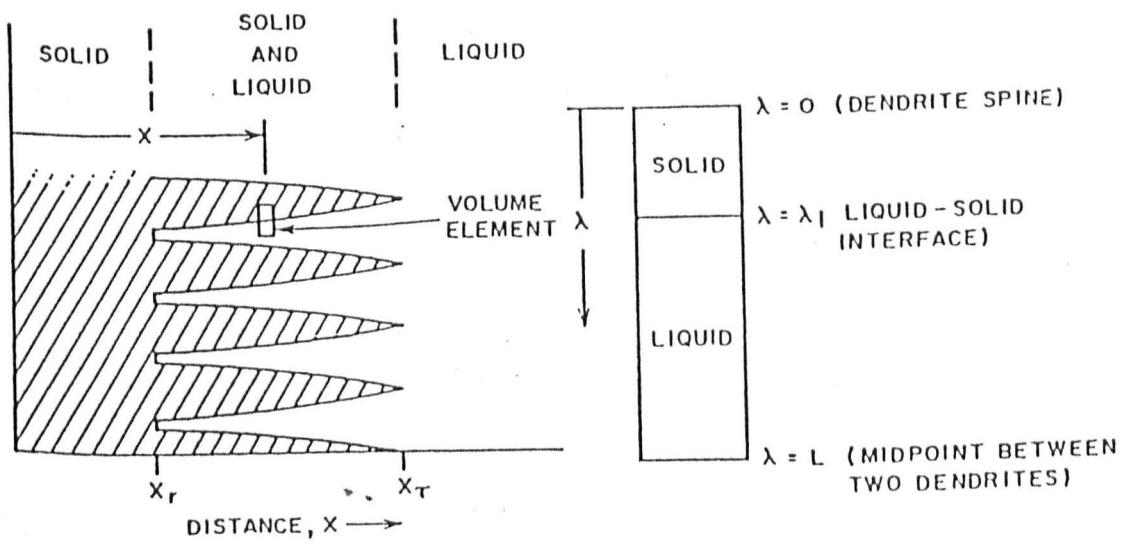
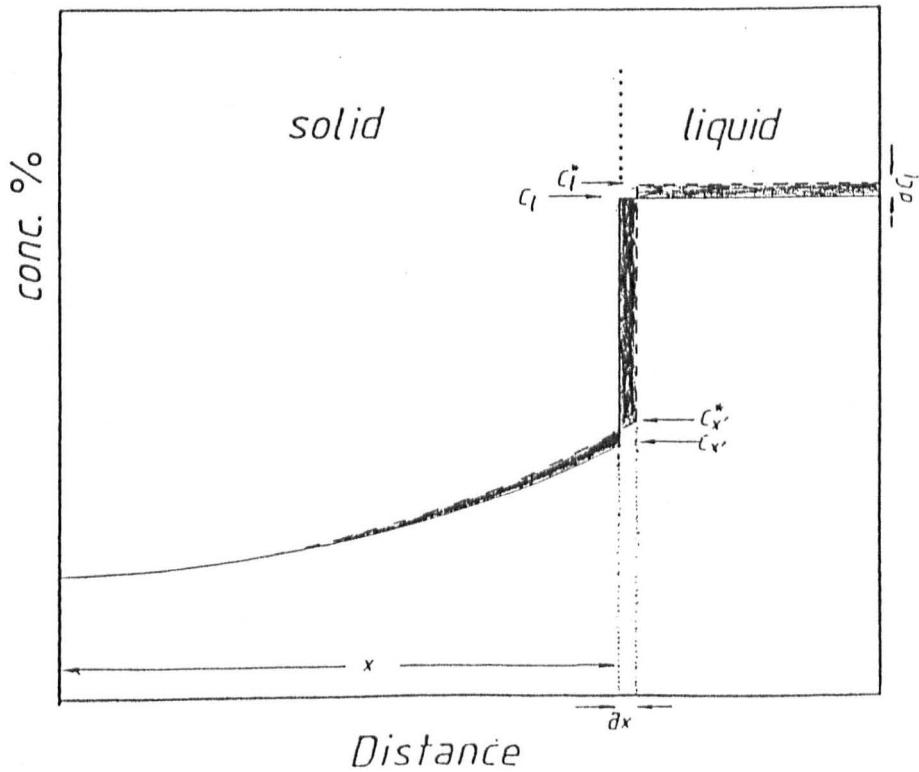


Figure 23

- a) Volume element modelled by Brody and Flemings from ref 74 (57)
- b) Dimentional form of volume element from centre of side arm
to centre of the liquid pool(57)



(a)



(b)

Figure 24

Arrangement of node points during finite difference calculations (57)

Figure 25

Volume element for side arm coarsening model (57)

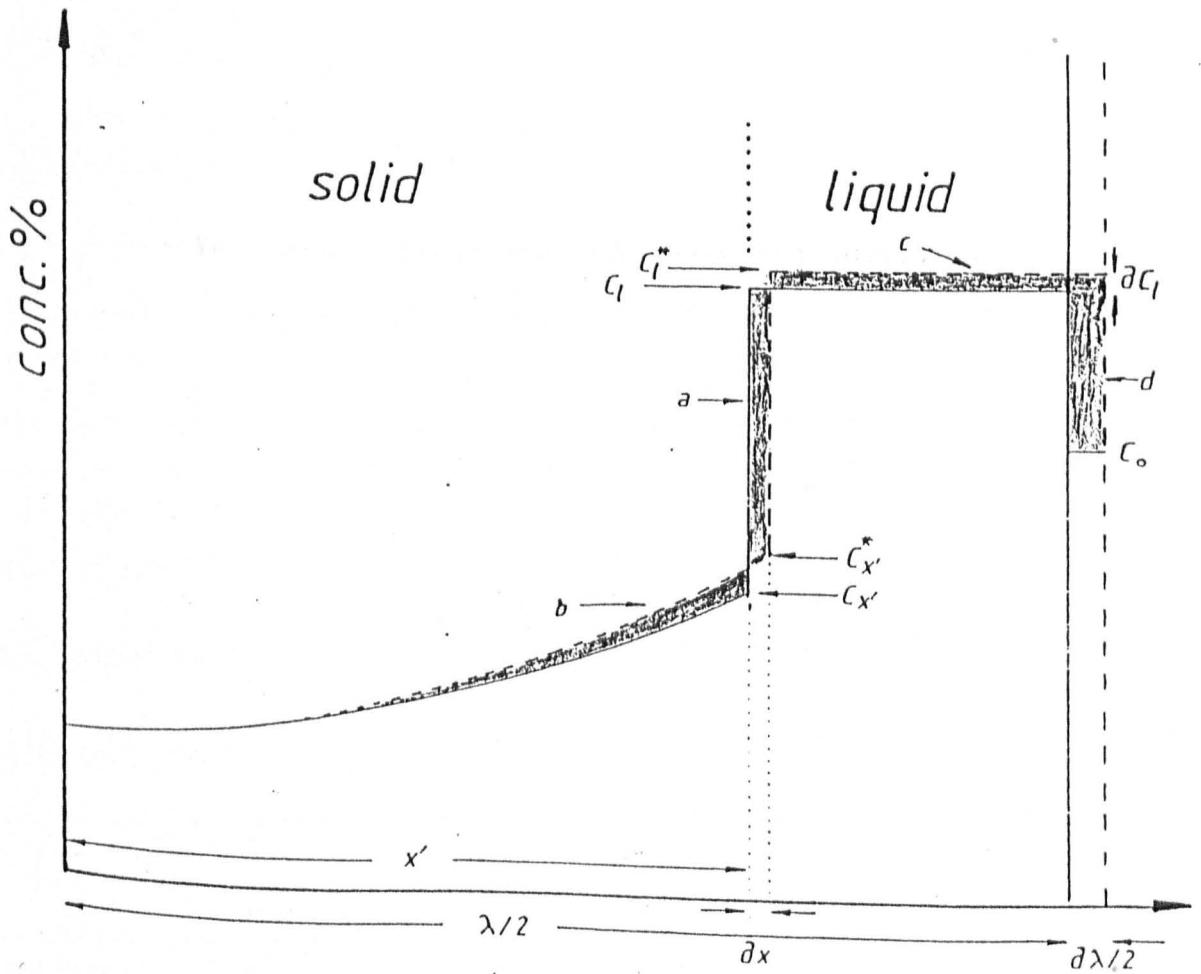
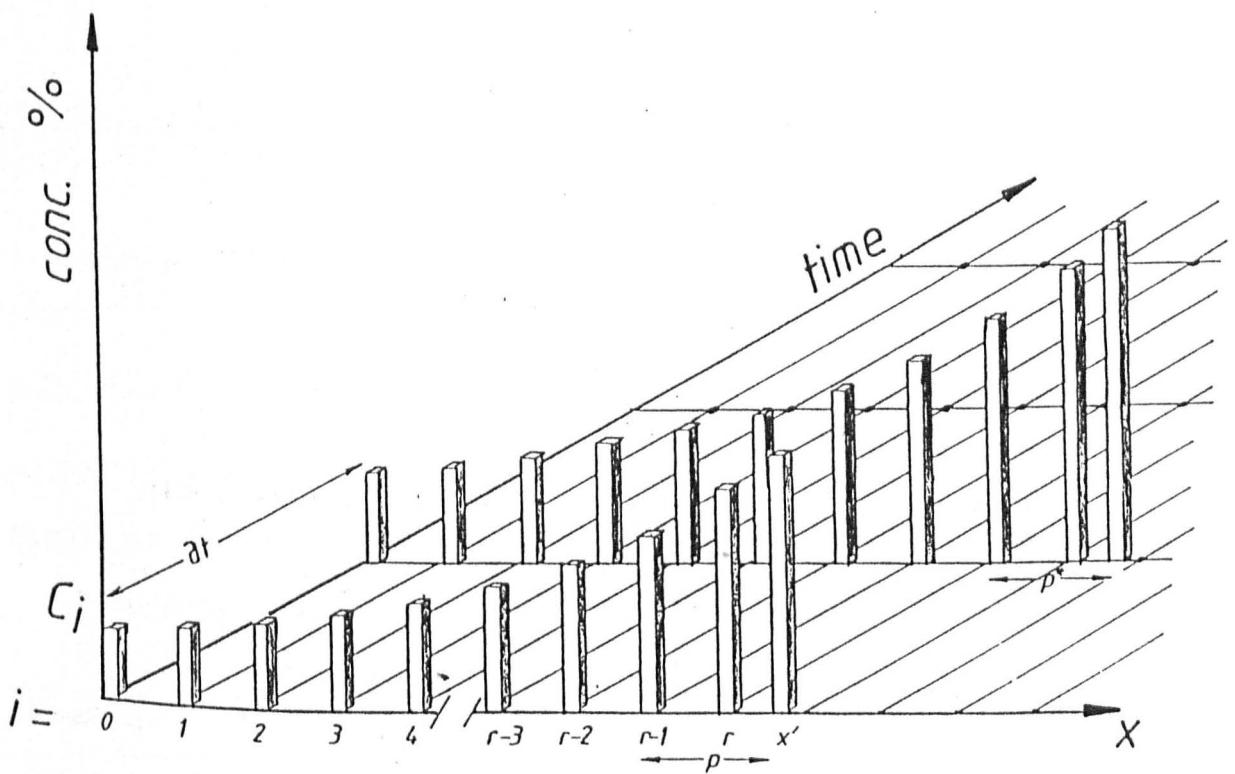


Figure 26

Photomicrograph of the longitudinal section of quenched 0.8 % C showing the high segregated lines between primary arms and the morphological change of secondary arms during solidification

0.8 % C - 1.6 % Mn - Fe

Growth rate	1.5 mm/min
Temperature gradient in liquid	8.4 C/mm
Magnification	X 25.7

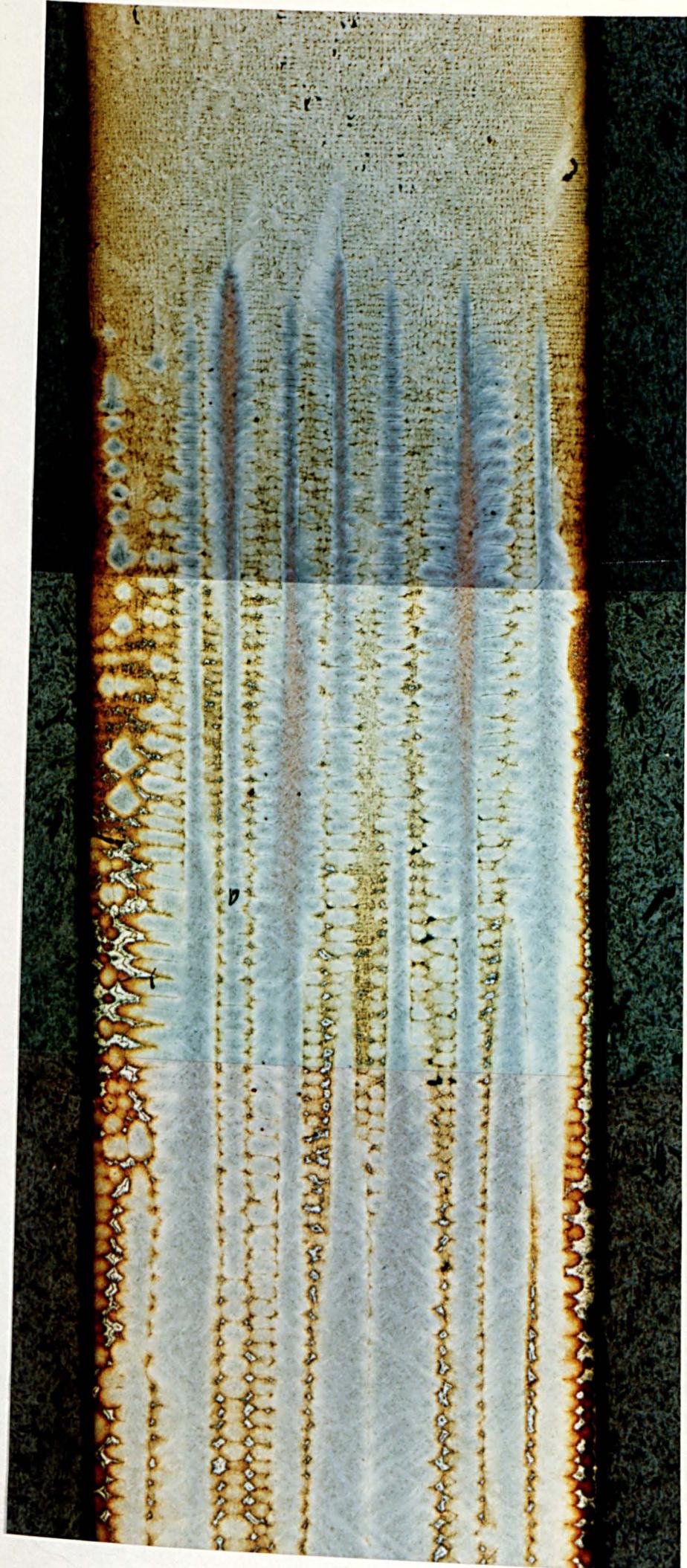




Figure 27

Photomicrograph of the morphological change in secondary arms
as a result of high coalescence process leaving highly segregated
points between primary arms surrounded by secondaries

0.8 % C - 1.6 % Mn - Fe

Growth rate	1.5 mm/min
Temperature gradient in liquid	8.4 C/mm
Magnification	X 137.5

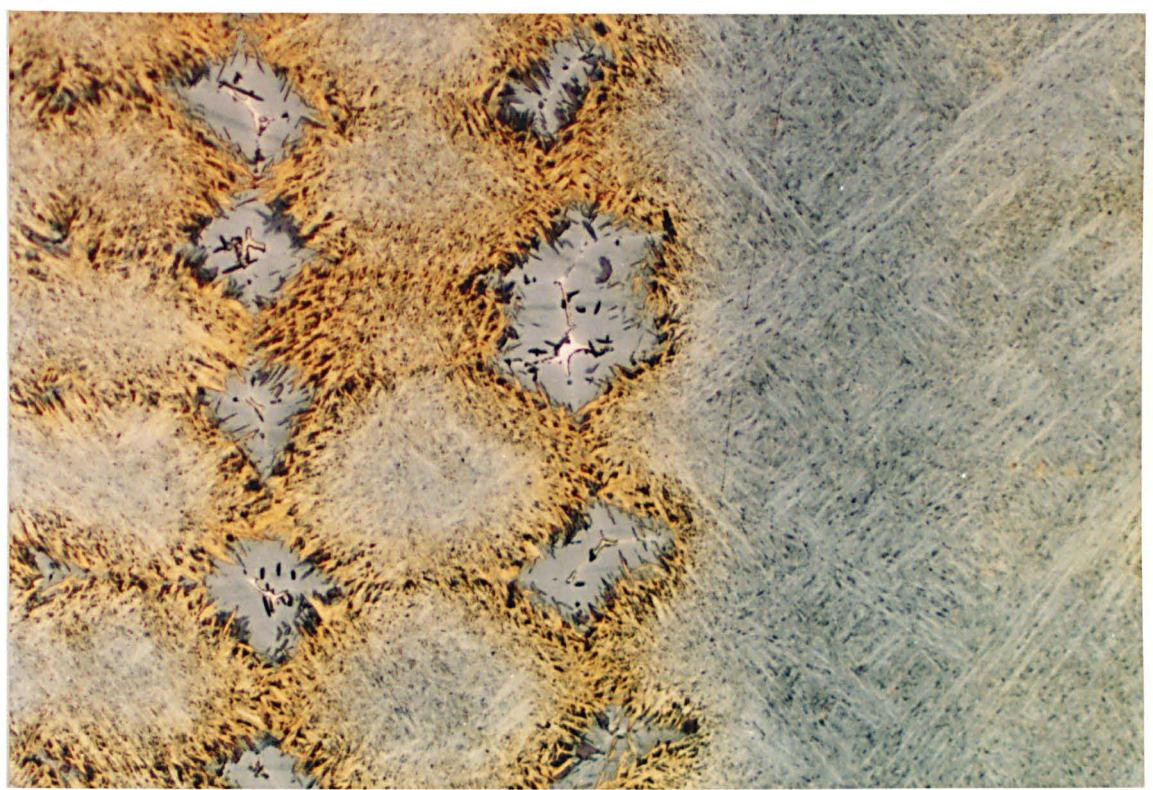
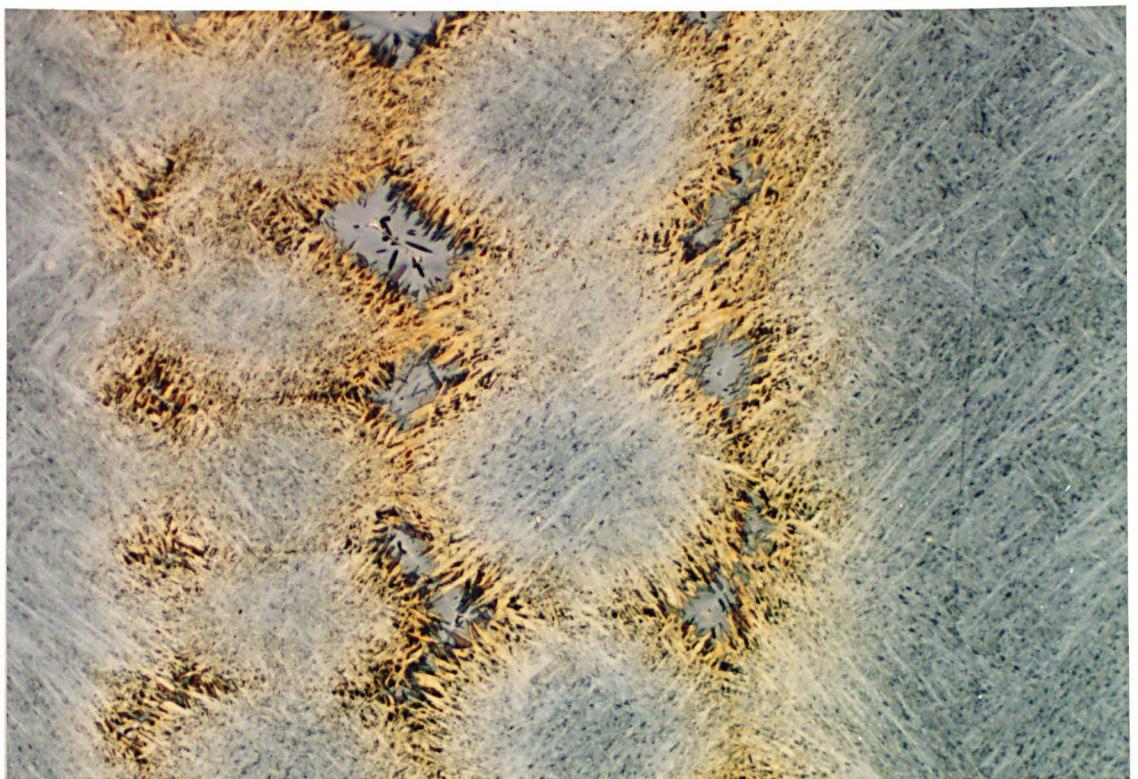


Figure 28

Photomicrograph of the longitudinal section of quenched 0.8 % C showing the highly segregated lines between primary arms and the secondary arm coarsening during solidification

0.8 % C - 1.6 % Mn - Fe

Growth rate 6 mm/min

Temperature gradient in liquid 7.2 C/mm

Magnification X 21

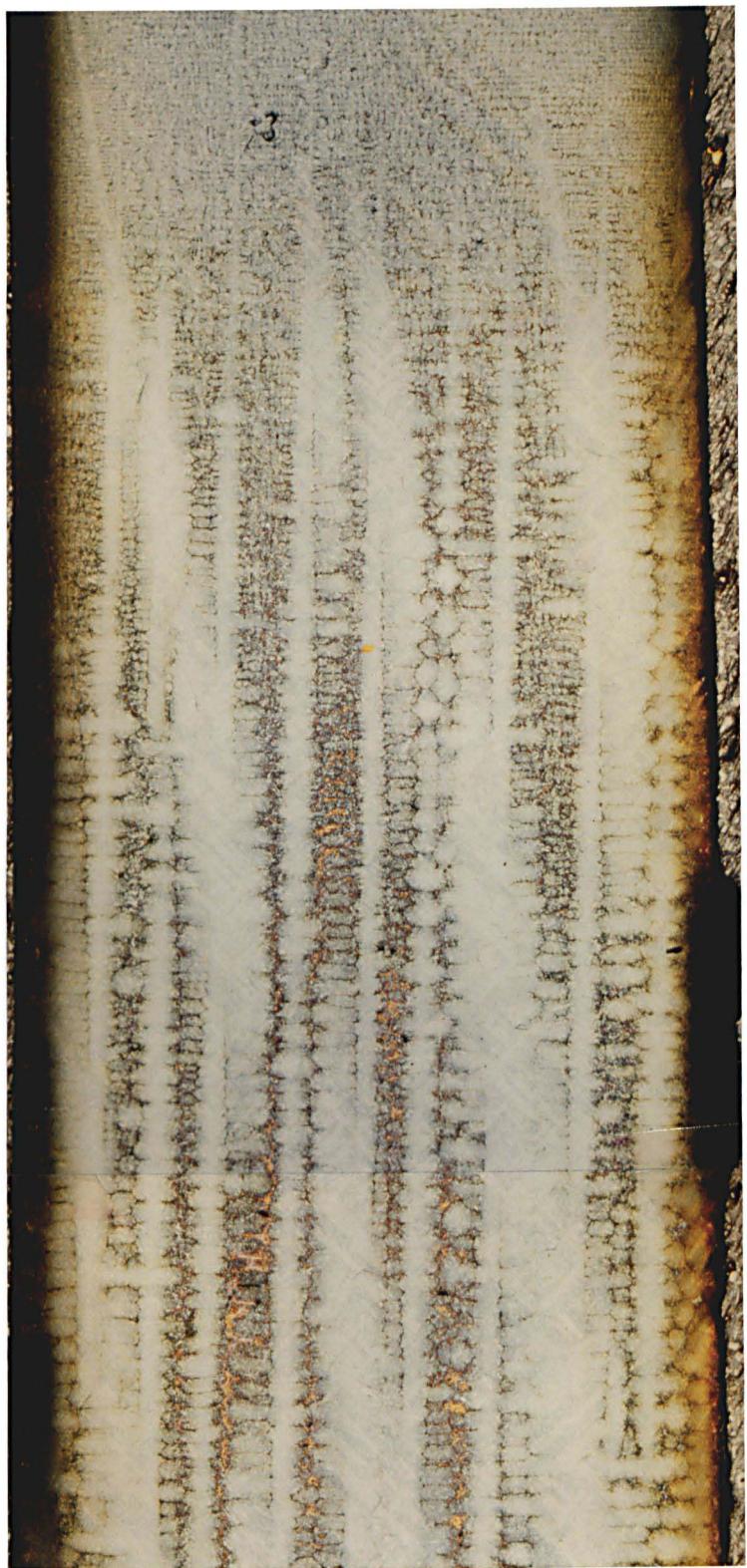


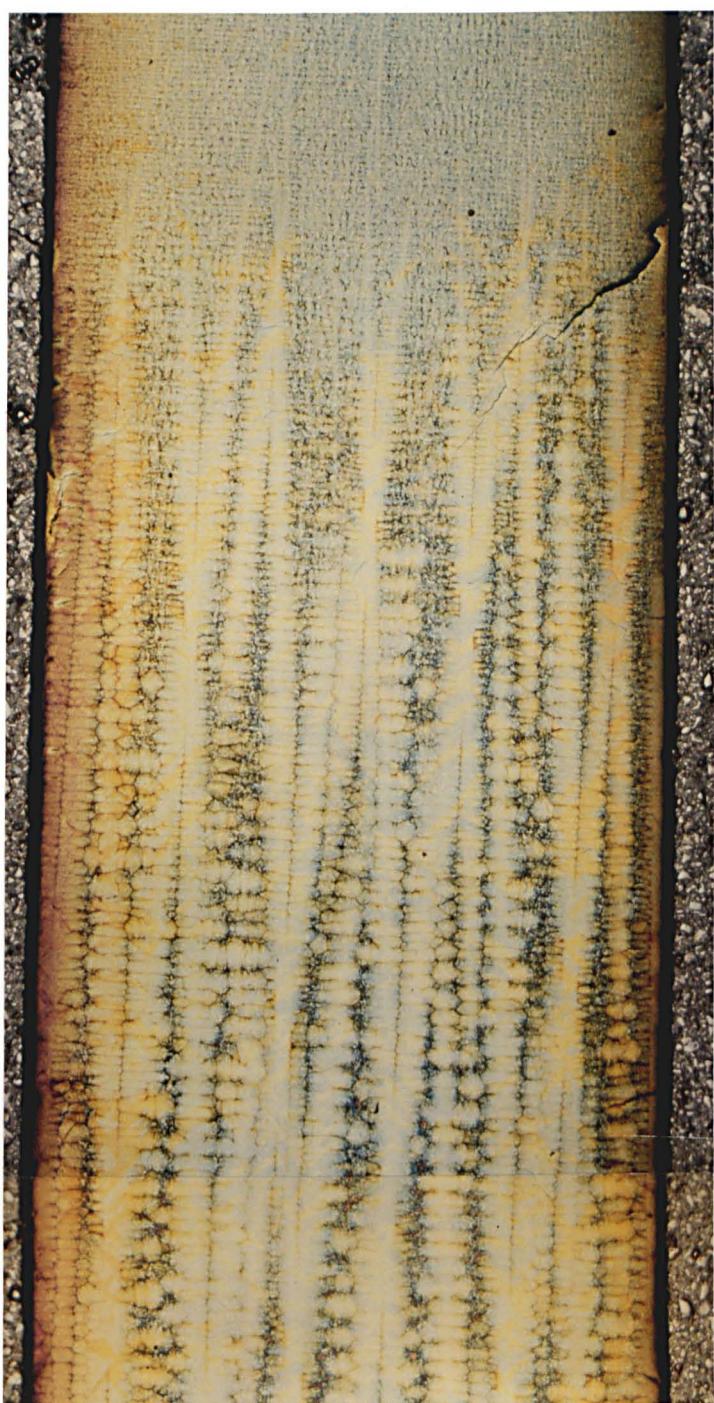


Figure 29

Photomicrograph of the longitudinal section of quenched 0.8 % C showing the highly segregated lines between primary arms and the secondary arm coarsening during solidification

0.8 % C - 1.6 % Mn - Fe

Growth rate	15 mm/min
Temperature gradient in liquid	5.9 C/mm
Magnification	X 21



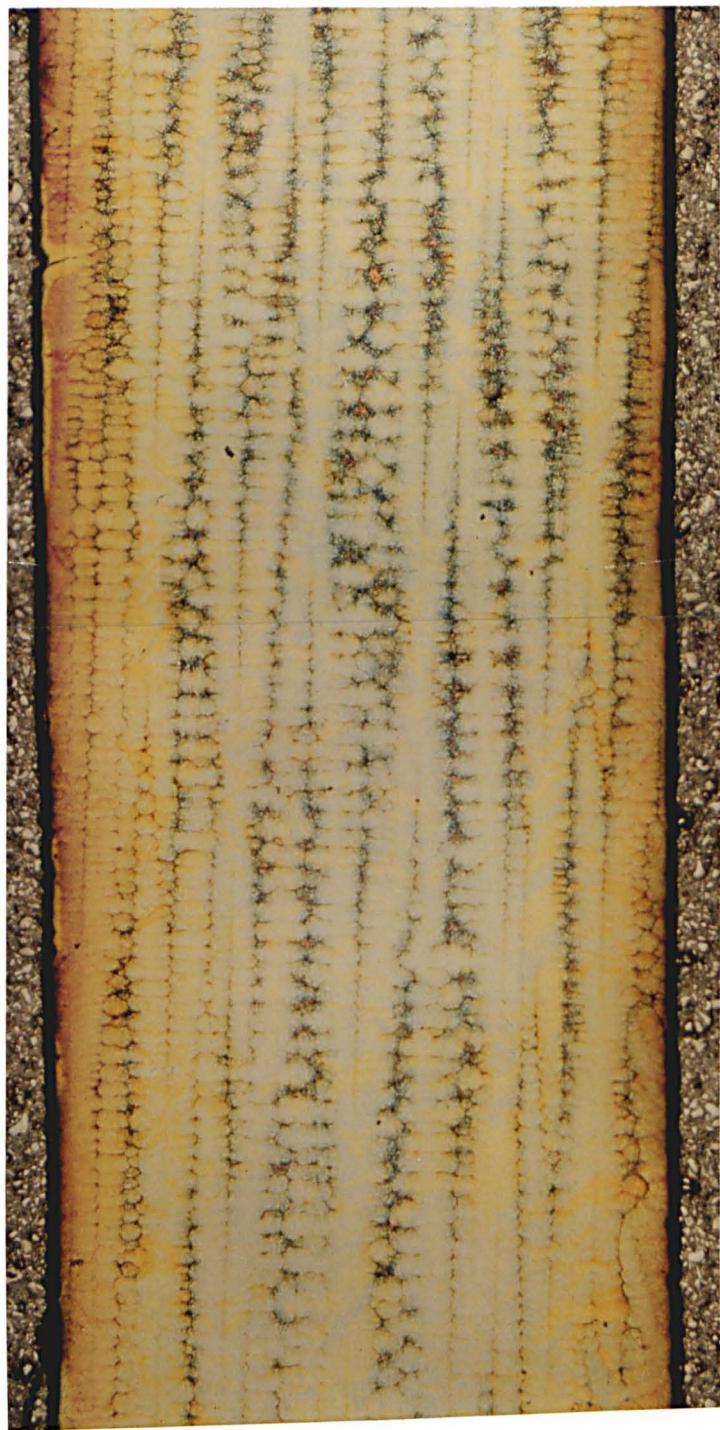


Figure 30

Photomicrograph of the longitudinal section of quenched low carbon alloy showing the highly segregated lines between primary arms and the poor developed secondary arms in the short solidification range

0.1 % C - 1.6 % Mn - Fe

Growth rate	6 mm/min
Temperature gradient in liquid	7.2 C/mm
Magnification	X 21



Figure 31.

Photomicrograph of the morphological change in secondary arms as a result of high coalescence and back diffusion process leaving highly segregated points between primary arms surrounded by secondary arms

0.1 % C - 1.6 % Mn - Fe

Growth rate 6 mm/min

Temperature gradient in liquid 7.2 C/mm

Magnification X 280

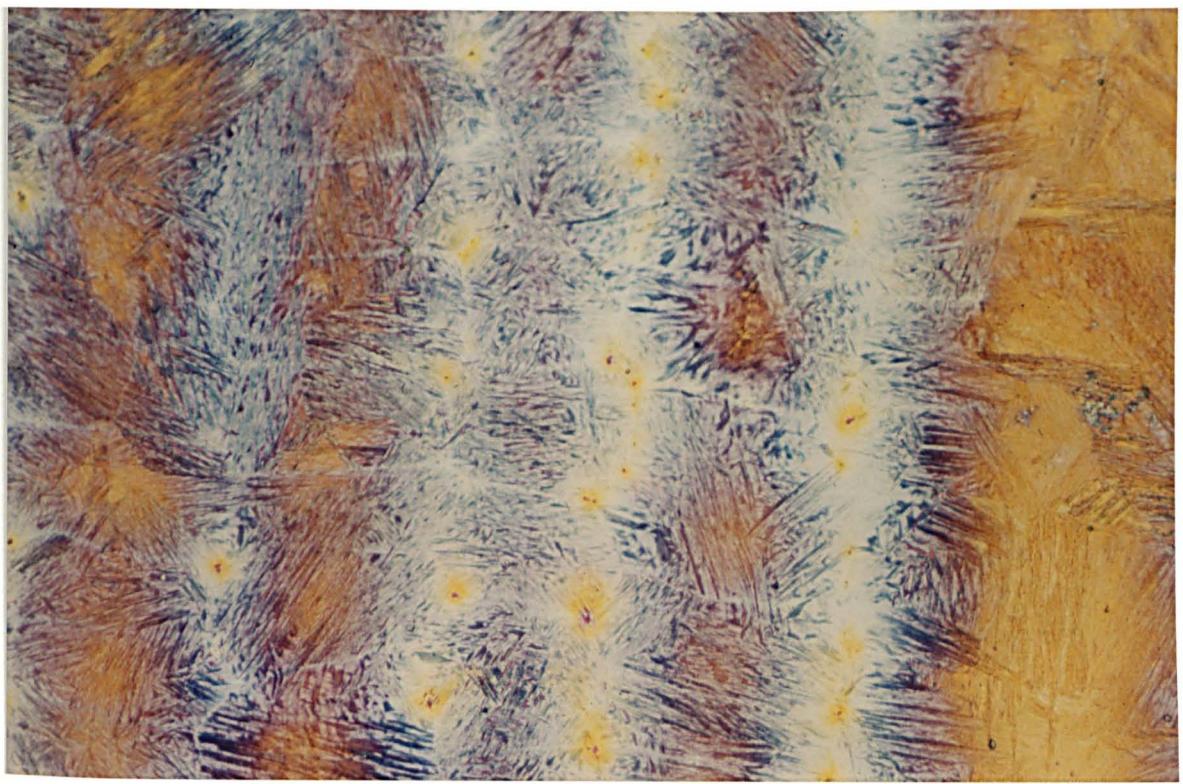
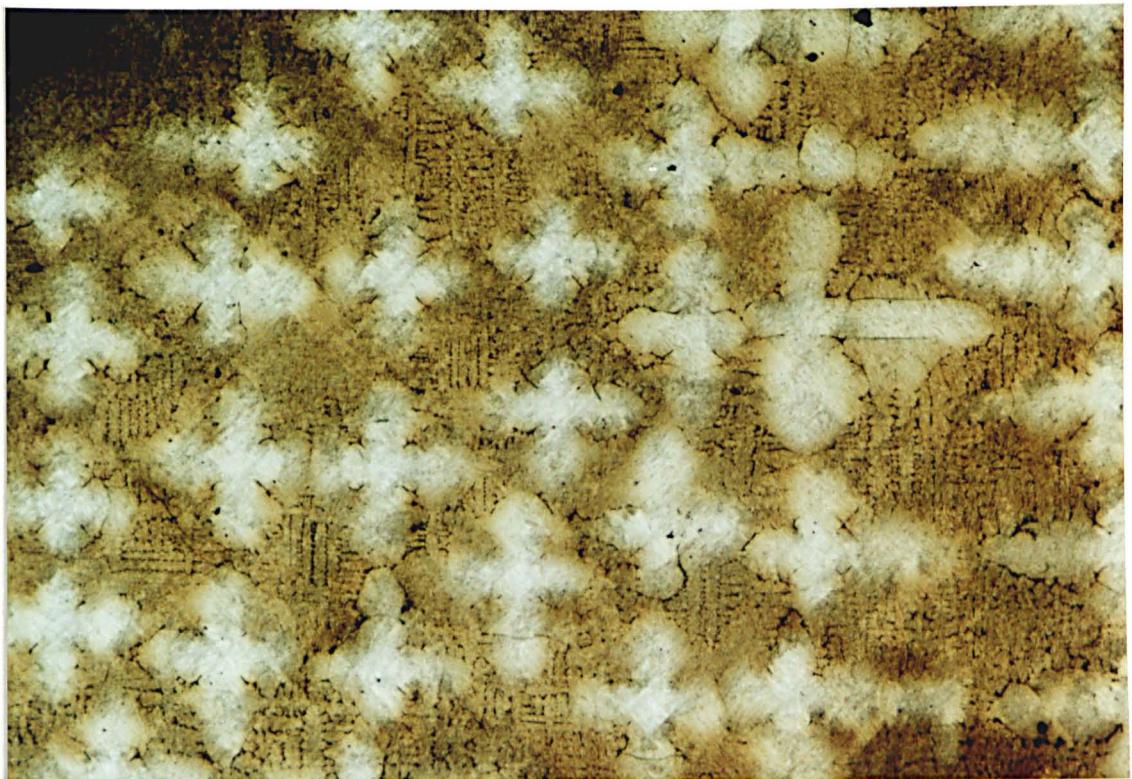


Figure 32

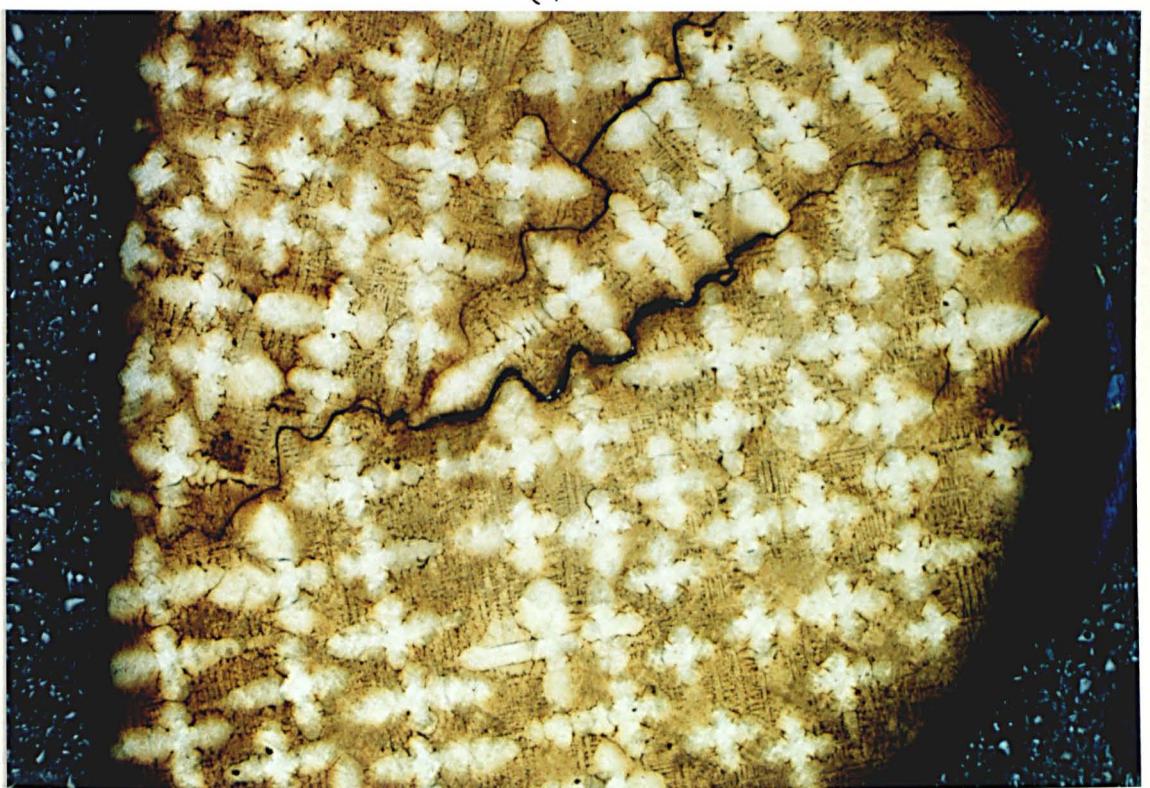
Photomicrograph of the transverse sections of figure 26 at the different distance behind tips showing the morphological change in the primary arms during solidification at the lowest growth rate (circular secondary arms)

0.8 % C - 1.6 % Mn - Fe

Growth rate	1.5 mm/min
Temperature gradient in liquid	8.4 C/mm
a- 0.5 mm behind tips	mag. 51.4
b- 0.5 mm behind tips	mag. 25.7
c- 2.7 mm behind tips	mag. 25.7
d- 5.9 mm behind tips	mag. 25.7
e- 10 mm behind tips	mag. 25.7
f- 20 mm behind tips	mag. 25.7



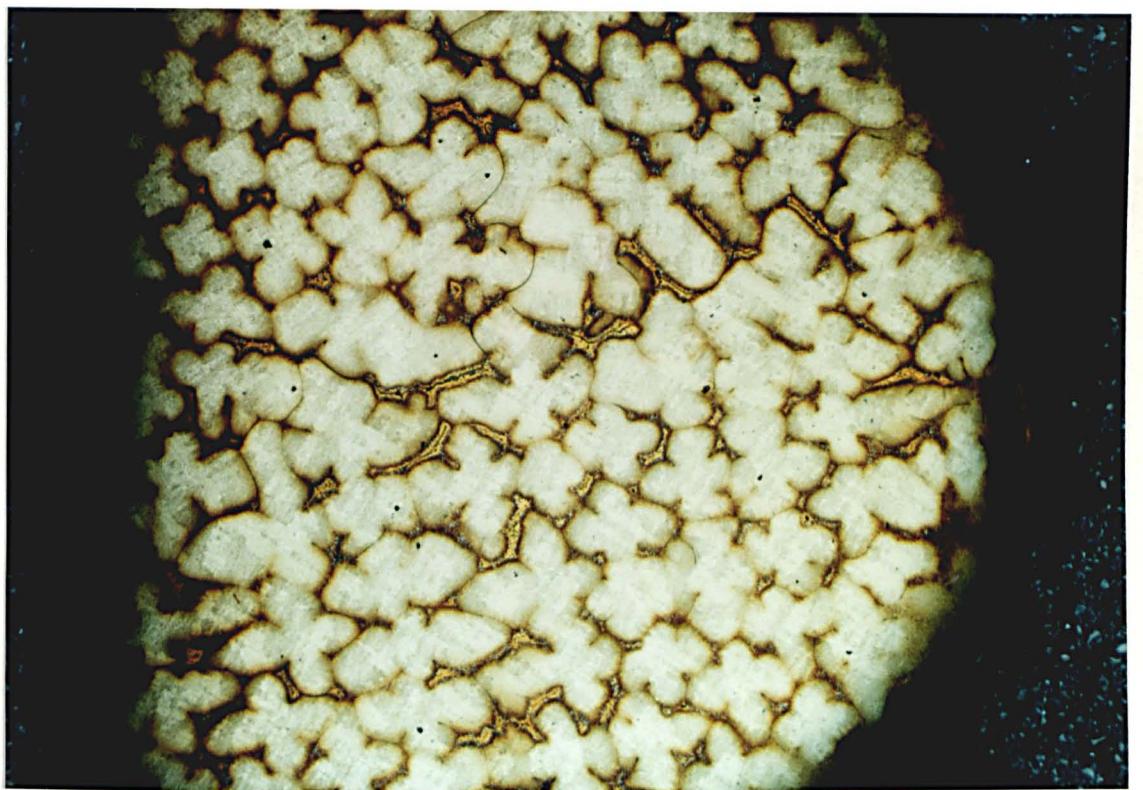
(a)



(b)



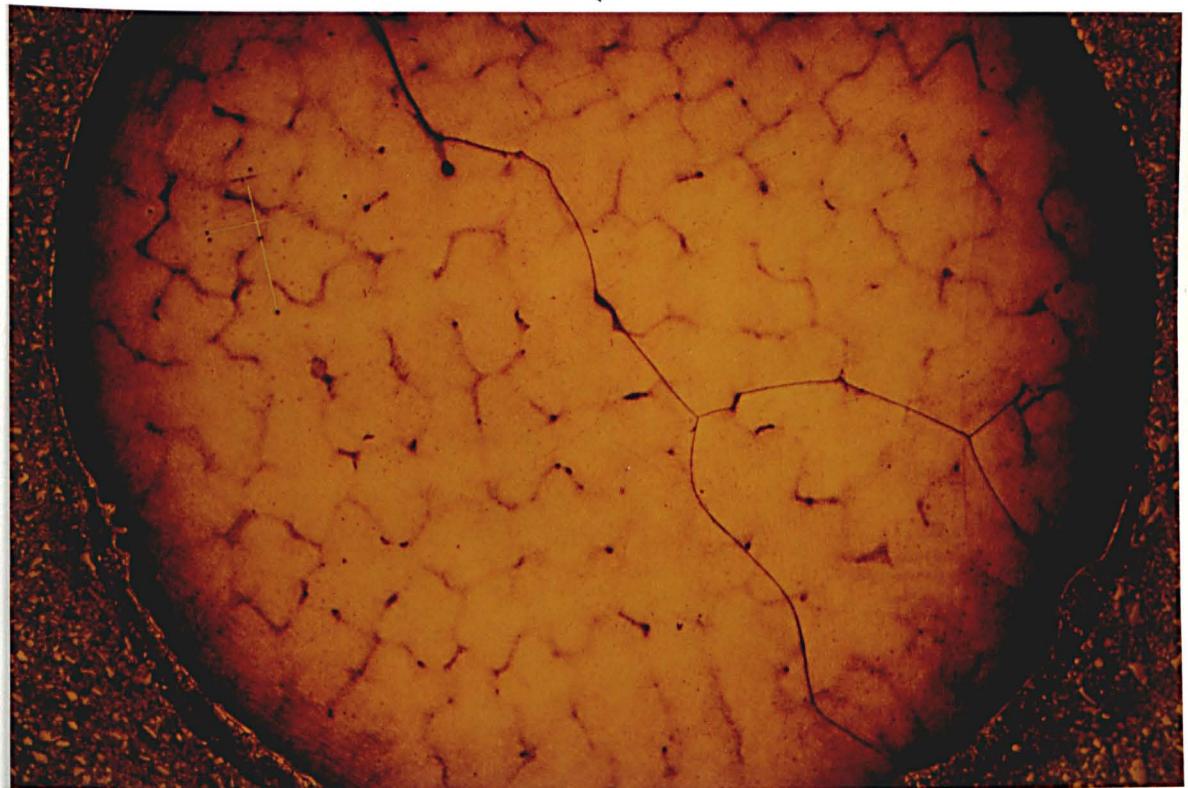
(c)



(d)



(e)



(f)

Figure 33 and 34

Photomicrographs of the transverse sections of the low carbon alloys showing the primary arm spacing with circular and poorly developed secondary arms at the lowest growth rate and indicating the delta ferrite - austenite phase transformation
(white - delta ferrite colour - austenite)

33) 0.1 % C - 1.6 % Mn - Fe

Growth rate	1.5 mm/min
Temperature gradient in liquid	8.4 C/mm
Magnification	X 142
Temperature	1480 C
Distance	4 mm

34) 0.2 % C - 1.6 % Mn - Fe

Growth rate	1.5 mm/min
Temperature gradient in liquid	10.7 C/mm
Magnification	X 71
Temperature	1465
Distance	3.75 mm.

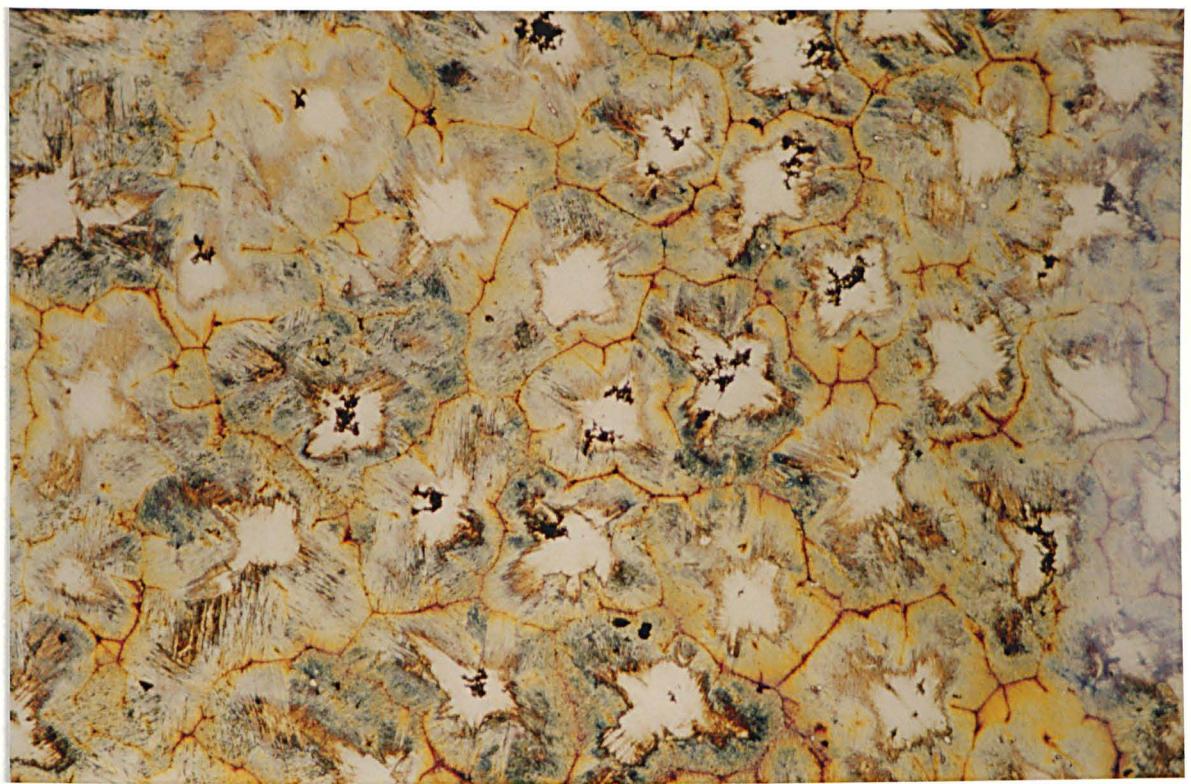
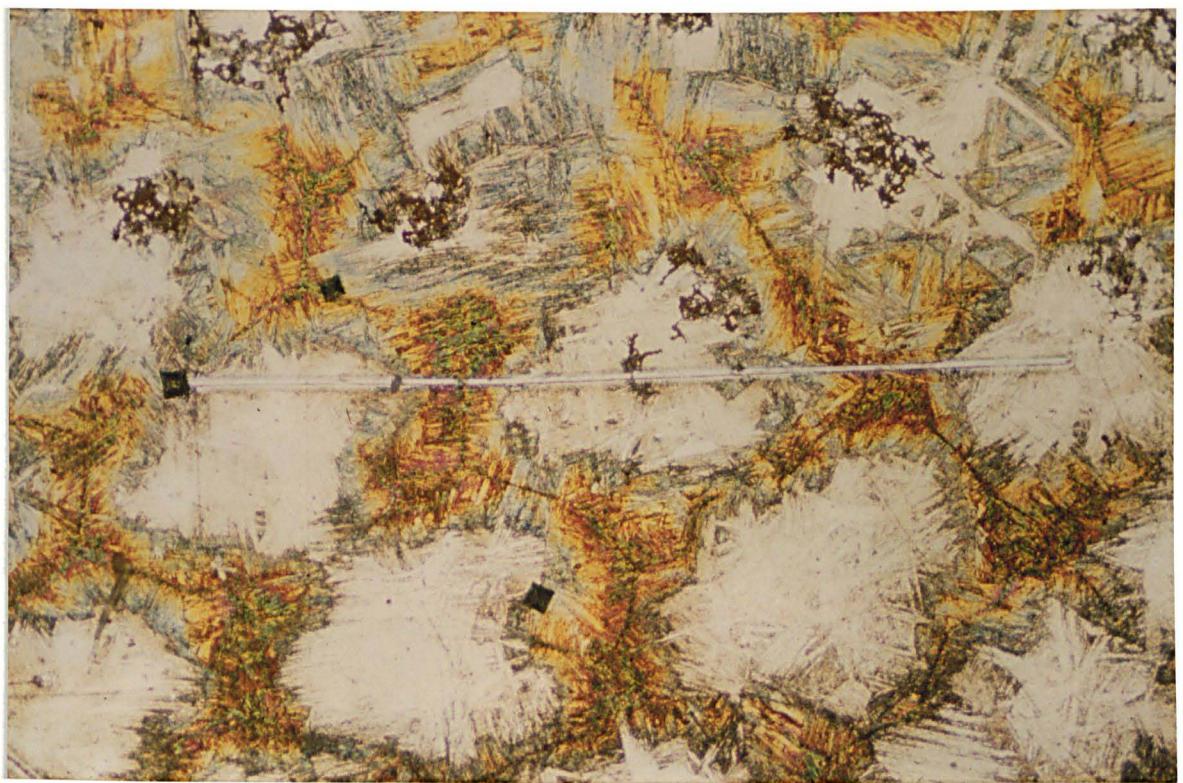


Figure 35

Photomicrograph of the transverse sections of quenched specimen showing the close packed morphological structure of primary arms (planar secondaries) at the high growth rate

0.8 % C - 1.6 % Mn - Fe

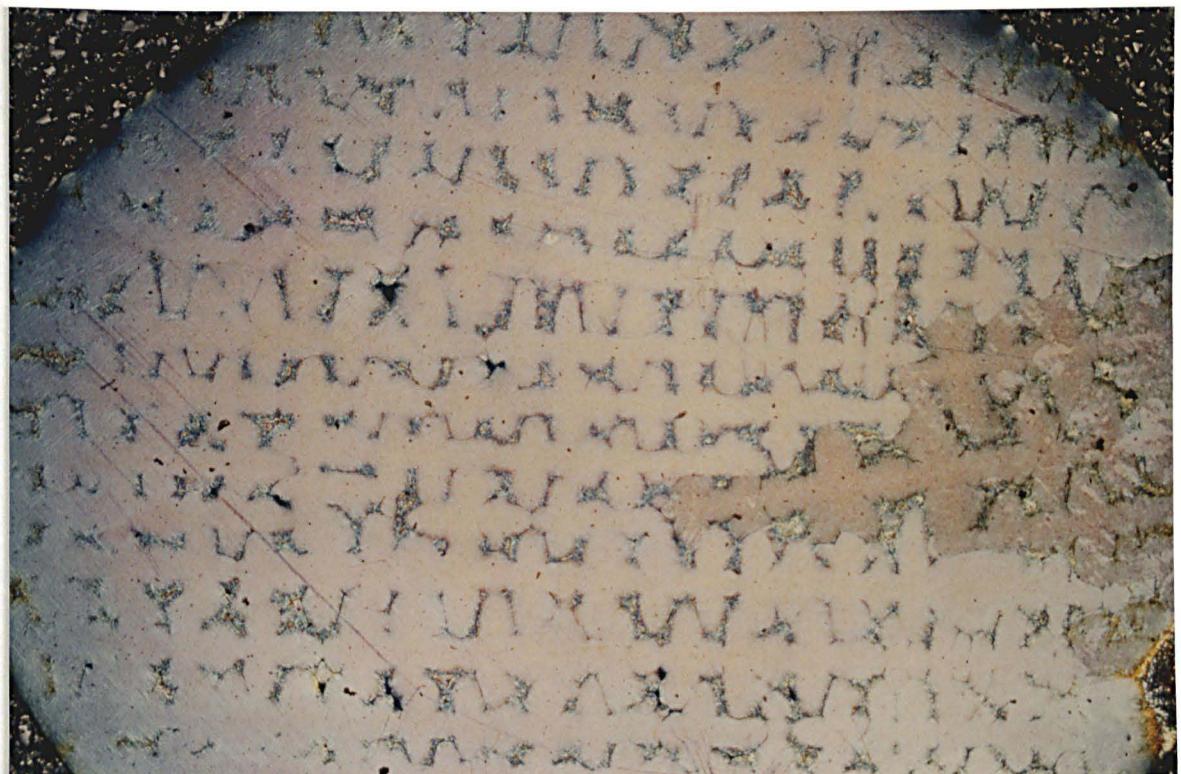
Growth rate 6 mm/min

Temperature gradient in liquid 5.5 C/mm

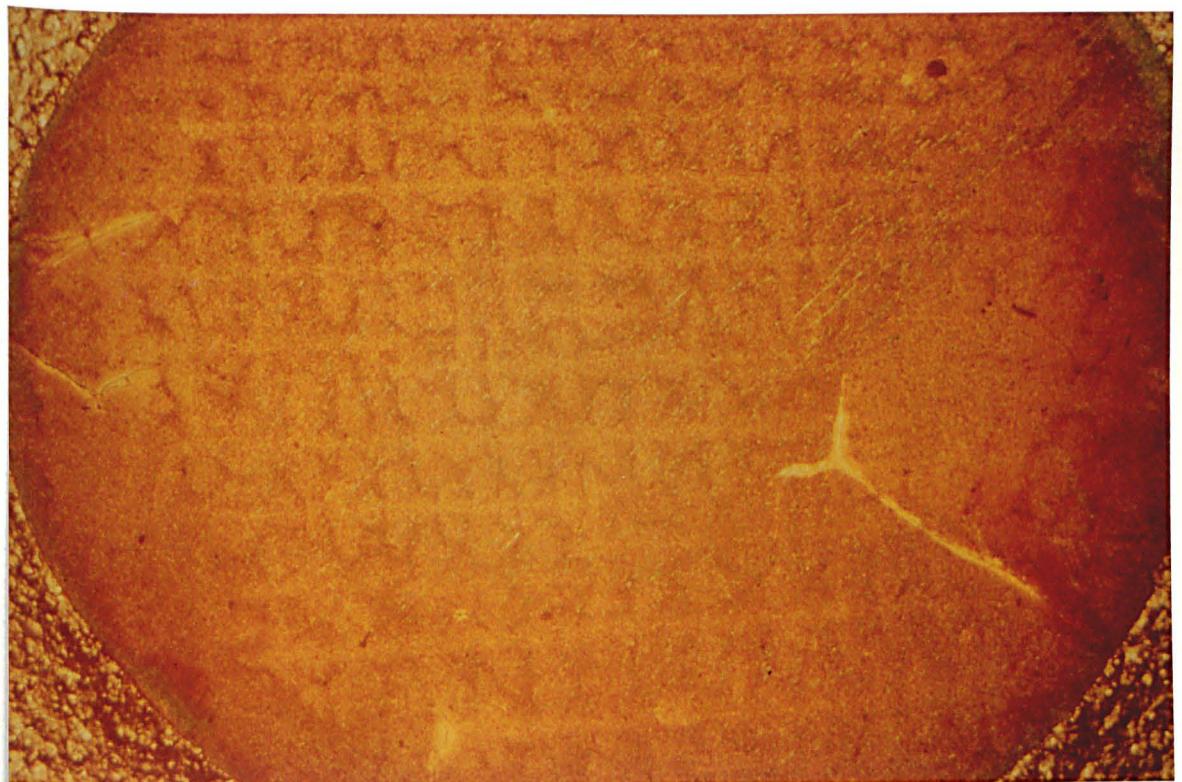
Magnification X 25

a- 14 mm behind tips

b- 28 mm behind tips



(a)



(b)

Figure 36

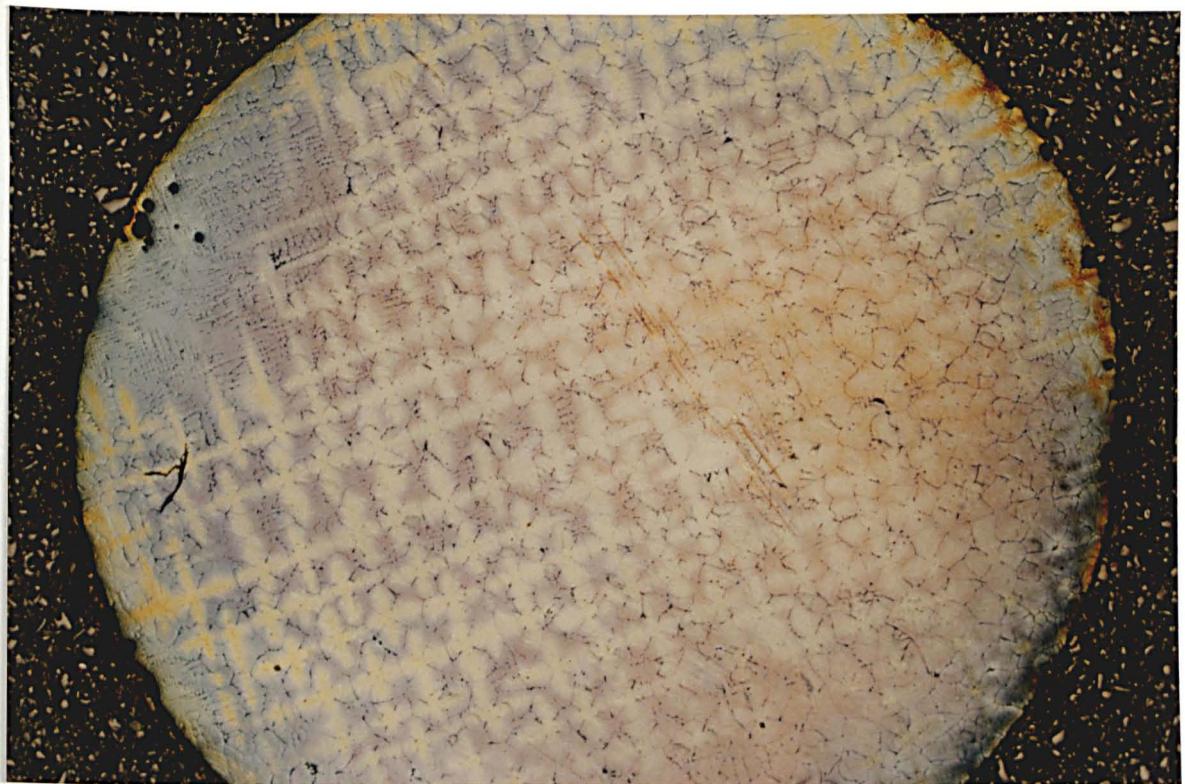
Photomicrograph of the close packed primary arm spacing morphology showing the effect of growth rate (comparing with figures 35 and 32)

0.8 % C - 1.6 % Mn - Fe

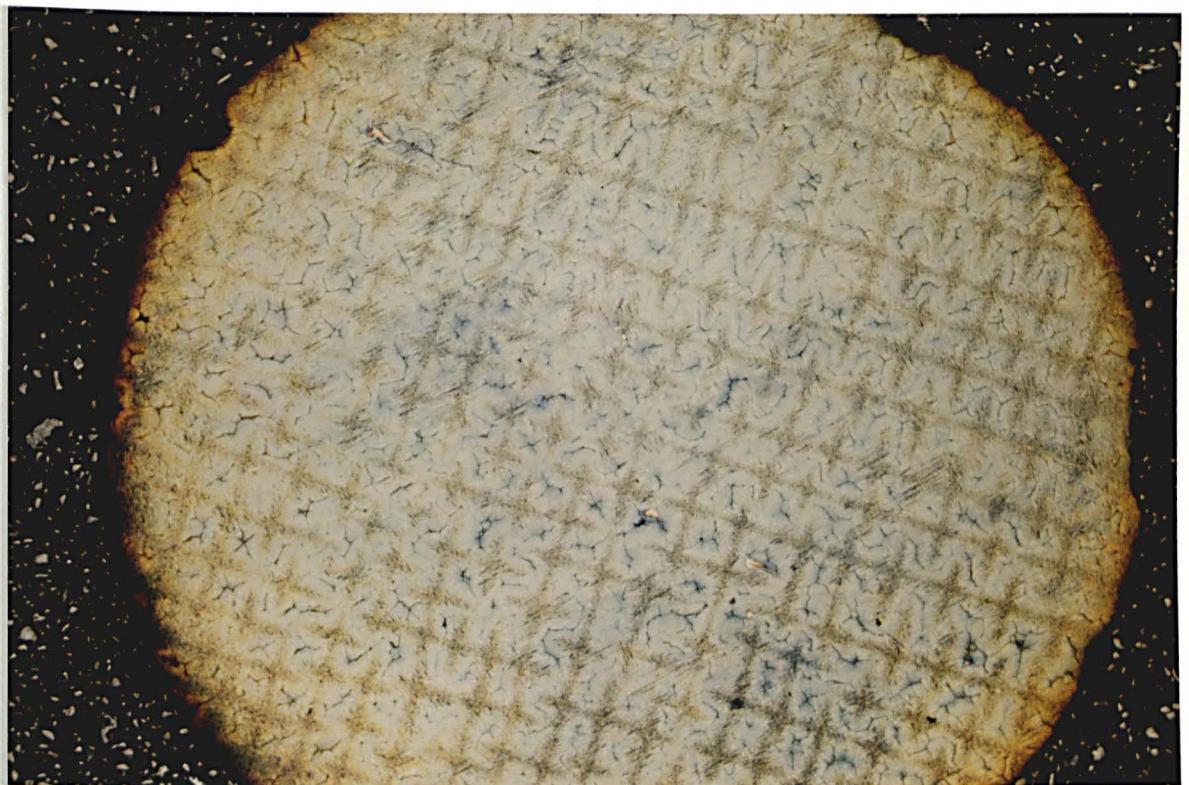
Growth rate	15 mm/min
Temperature gradient in liquid	5.9 C/mm
Magnification	X 25

a- 1.5 mm behind tips

b- 19 mm behind tips



(a)



(b)

Figure 37

Photomicrograph of the planar [redacted] secondary arms at the high magnification

0.4 % C - 1.6 % Mn - Fe

Magnification

X 284

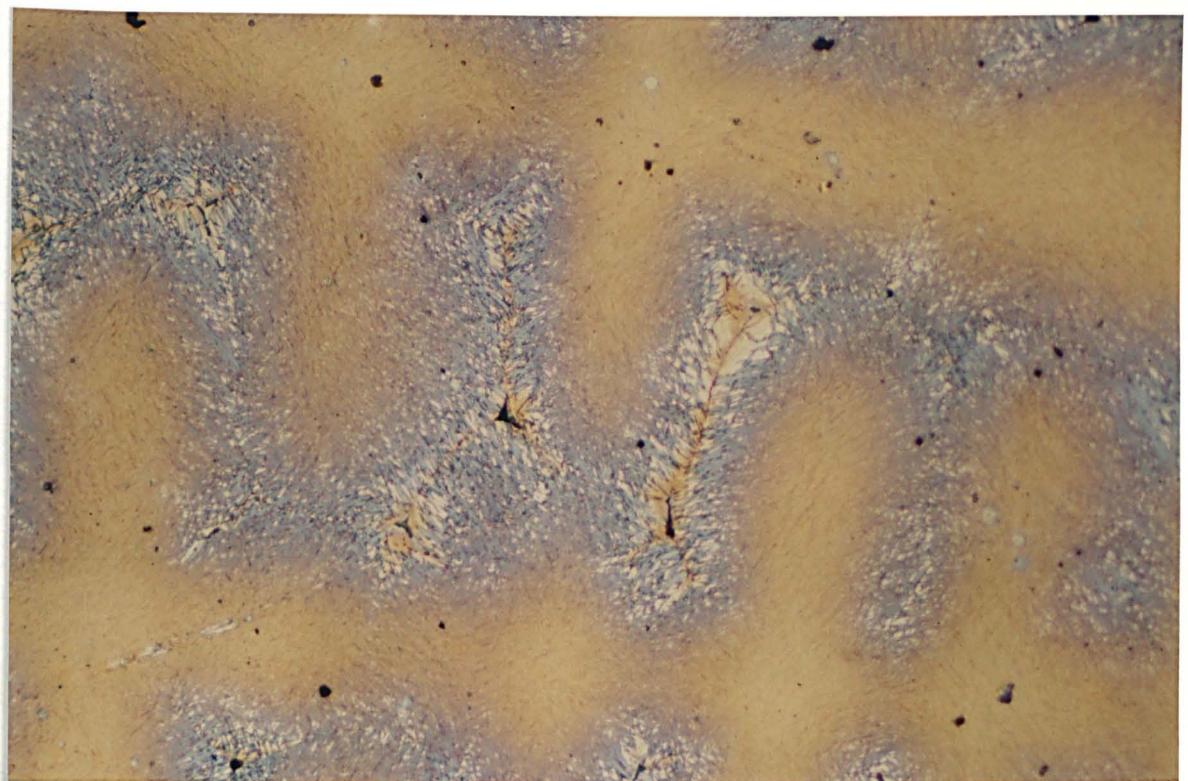


Figure 38

Photomicrographs of the transverse sections of primary arms spacing for low carbon steel showing the delta ferrite - austenite phase transformation during solidification at the different distance behind tips

0.1 % C - 1.6 % Mn - Fe

Growth rate 6 mm/min

Temperature gradient in liquid 7.2 C/mm

Magnification X 142

a- 3 mm behind tips at 1495 C

b- 8 mm behind tips at 1440 C

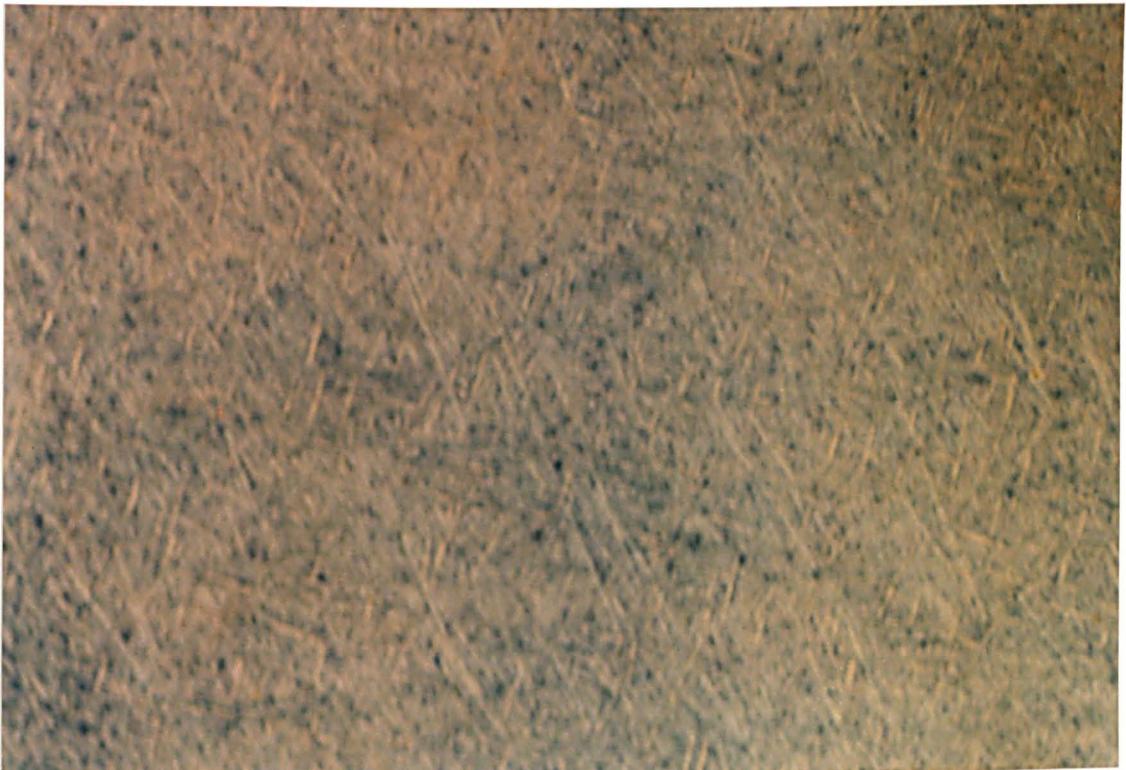
c- 14 mm behind tips at 1330 C



(a)



(b)



(c)

Figure 39

The change in the primary arm spacing as a function of temperature gradient in liquid and growth rate for different carbon content

a- 0.1 % C

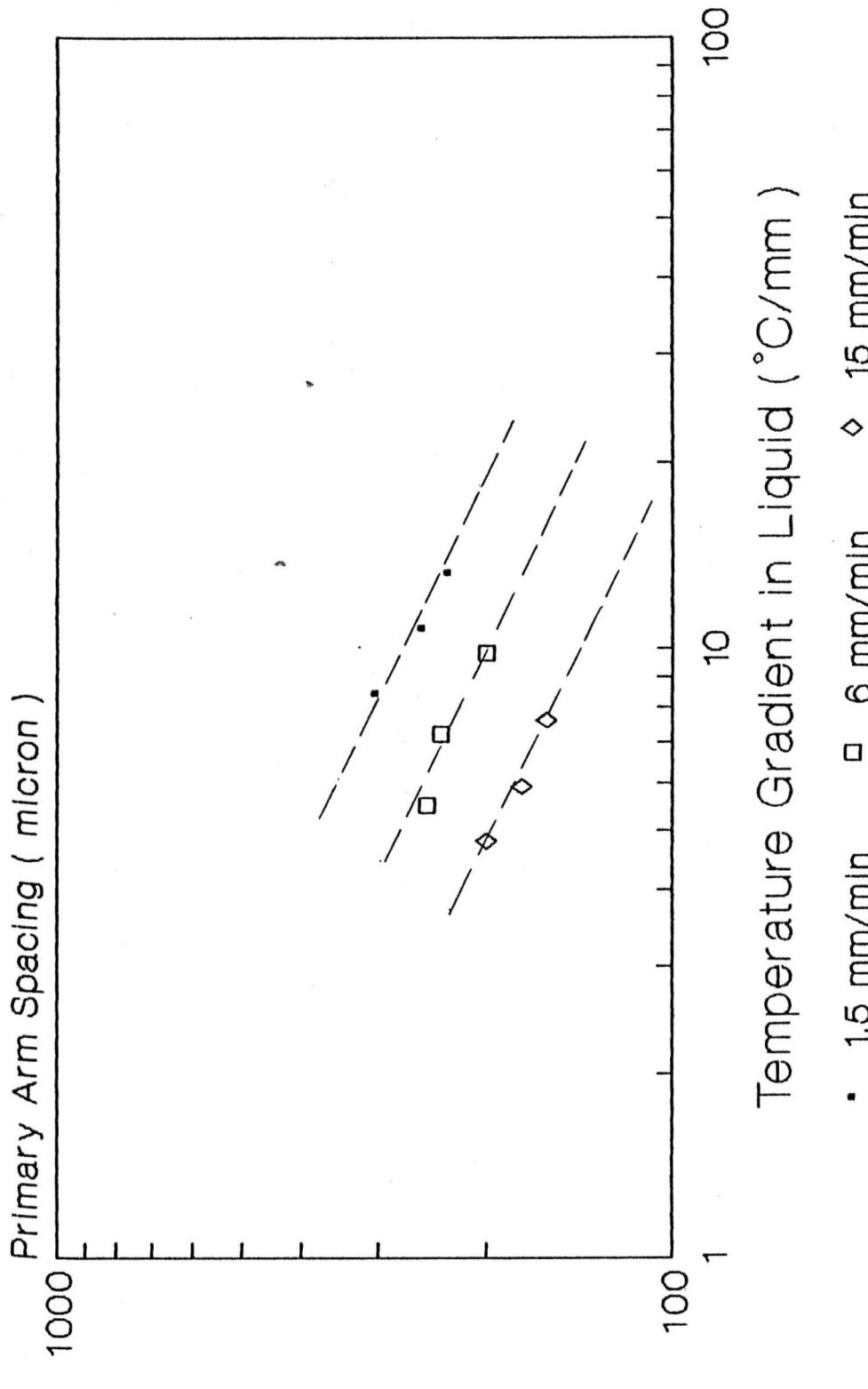
b- 0.2 % C

c- 0.4 % C

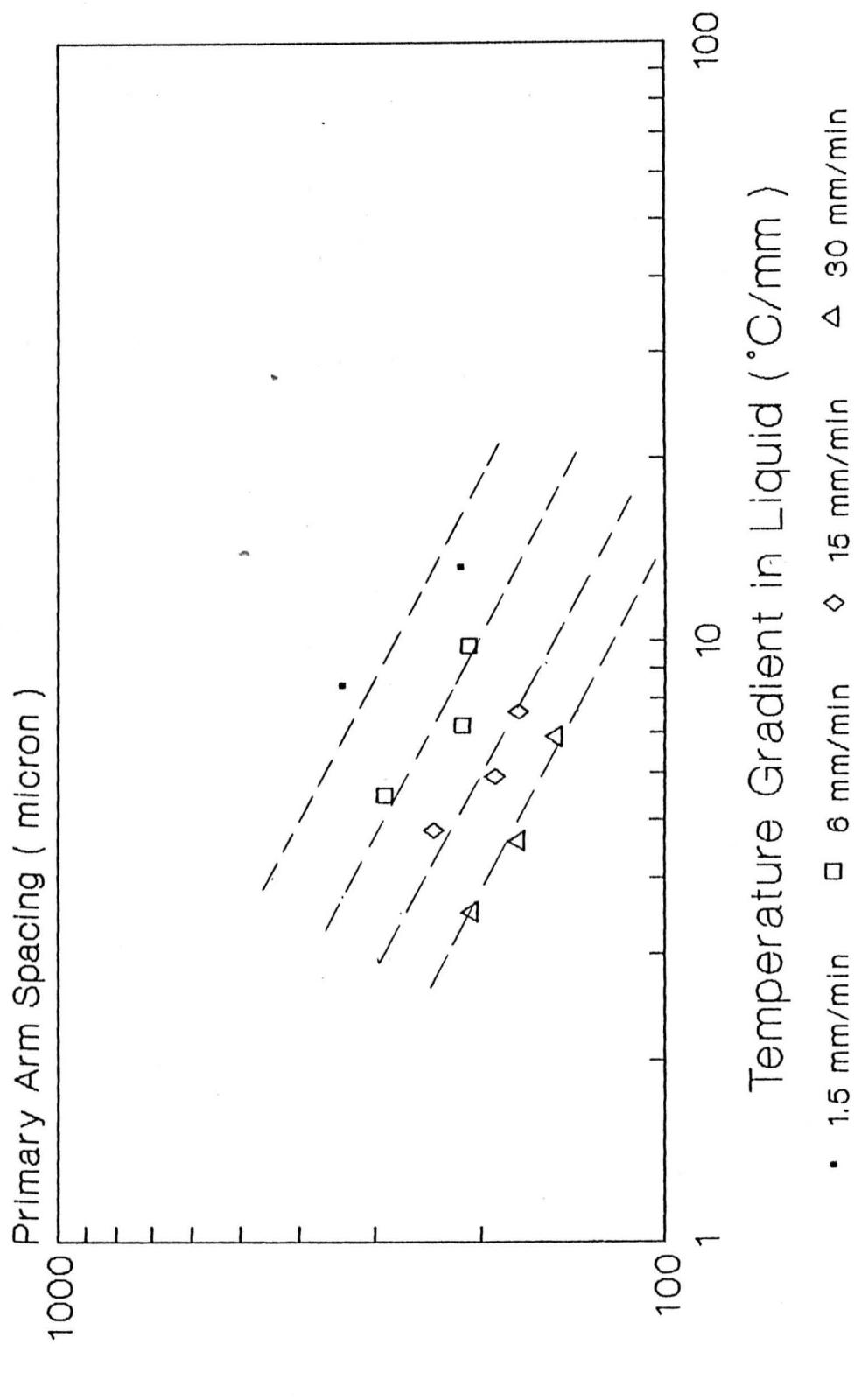
d- 0.8 % C

- - - - - 0.5 slope

(a)

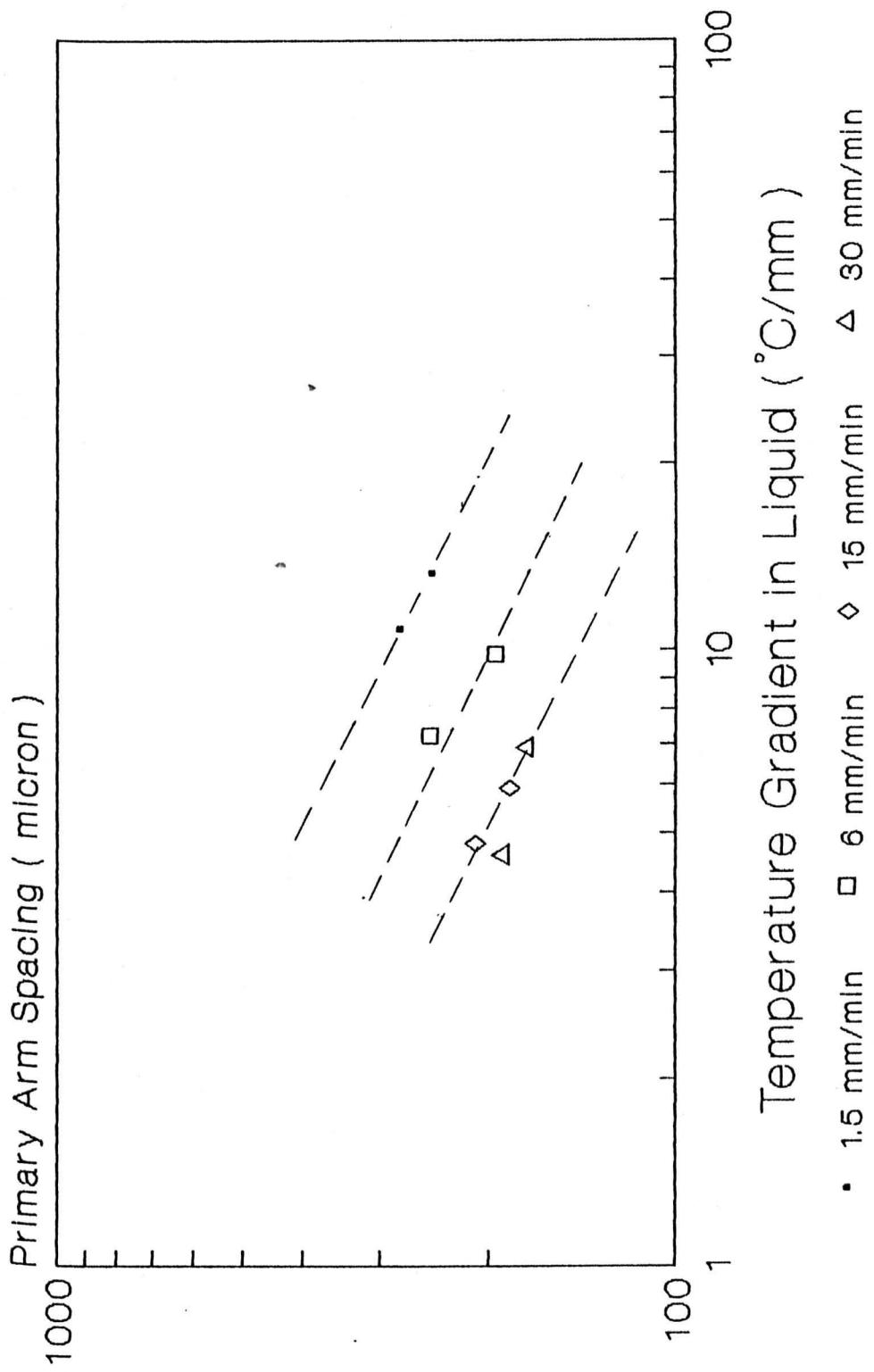


(b)



(c)

0.4 % C



(d)

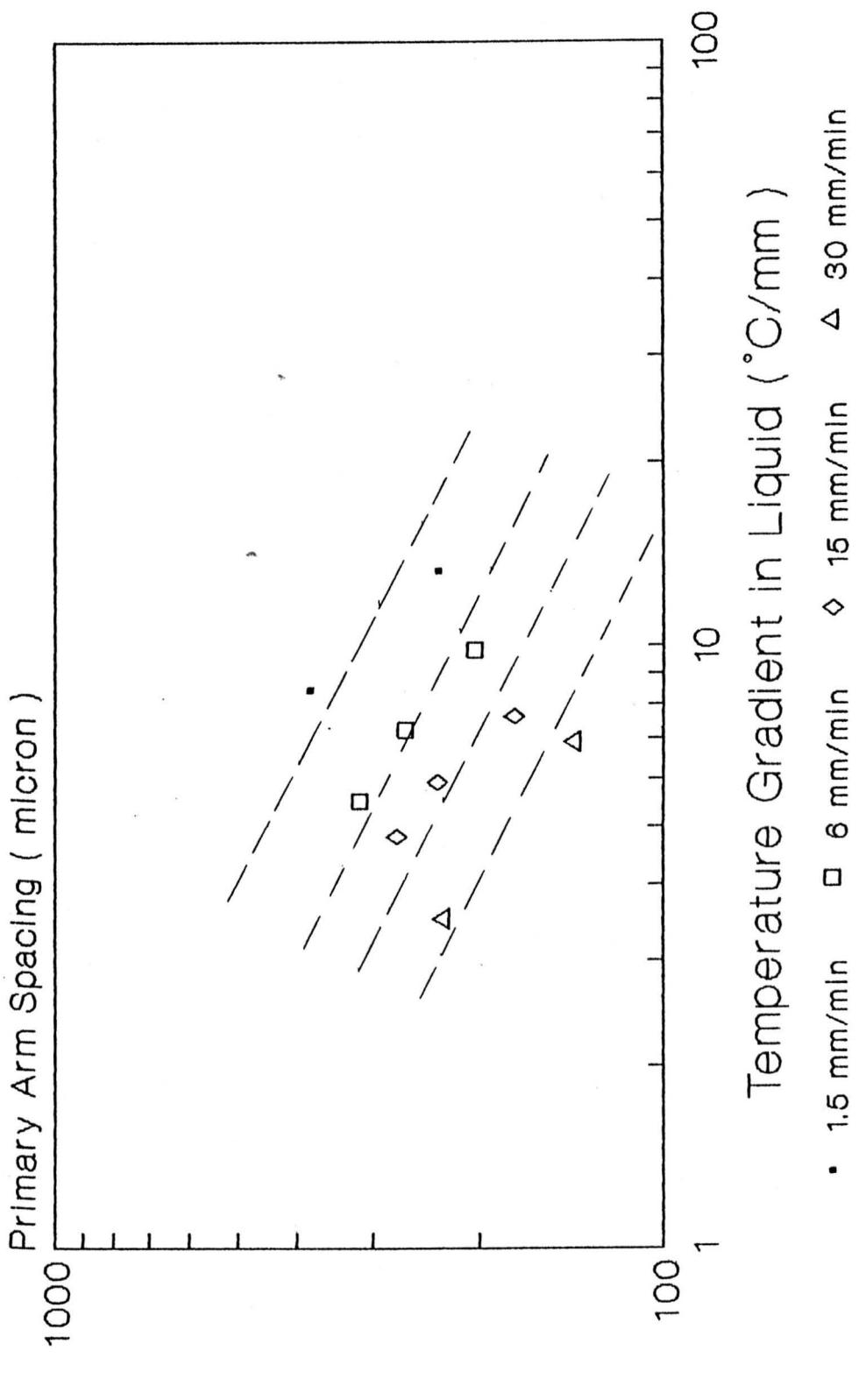


Figure 40

The change in primary arm spacing as a function of growth rate at the temperature gradient of 5.5 C/mm and 8 C/mm. Data are taken from the straight lines in figure 15-d. Experimental measurements near these gradients are also included on the figure. (0.8 % C - 1.6 % Mn - Fe)

- - - - - 0.4 slope

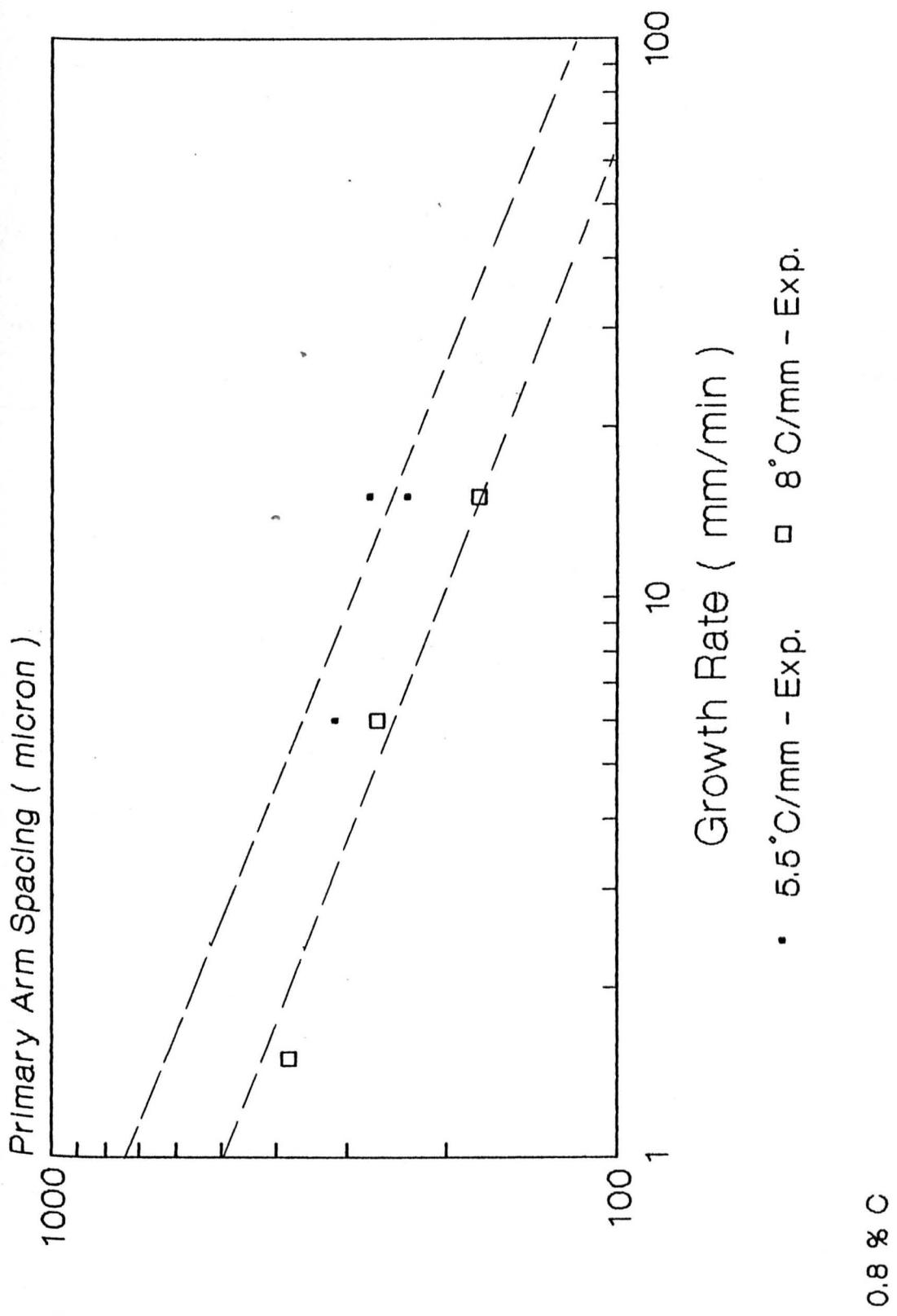
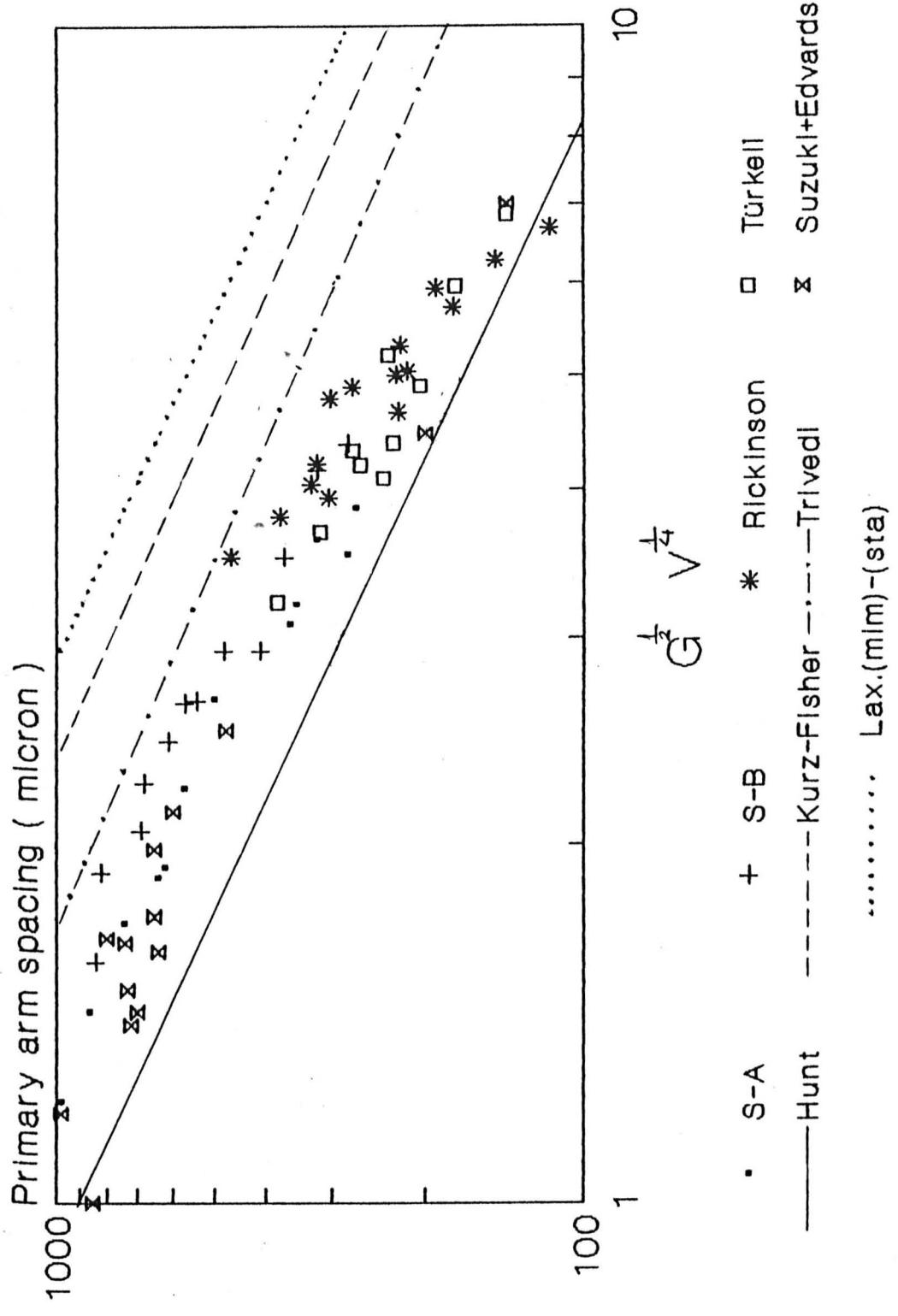


Figure 41

Comparison between theoretical prediction and experimental data for same kind of alloy groups

S-A Jacobi and Schwerdtfeger (46)	0.6 % C - 1.1 % Mn - Fe
S-B Jacobi and Schwerdtfeger (46)	1.5 % C - 1.15 % Mn - Fe
Rickinson (44)	1 % C - 1.4 % Cr - Fe
Turkeli (present work)	0.8 % C - 1.6 % Mn - Fe
Suziki and Nagoaka (43)	0.4 % C - 1 % Cr - 0.25 % Mo - Fe
Edvardsson et al. (48)	0.4 % C - 1.6 % Mn - Fe
Hunt equation prediction for 0.8 % C	
Kurz-Fisher equation prediction for 0.8 % C	
Trivedi equation prediction for 0.8 % C	
Laxmanan's minimum undercooling and stability equation prediction for 0.8 % C	



०८०

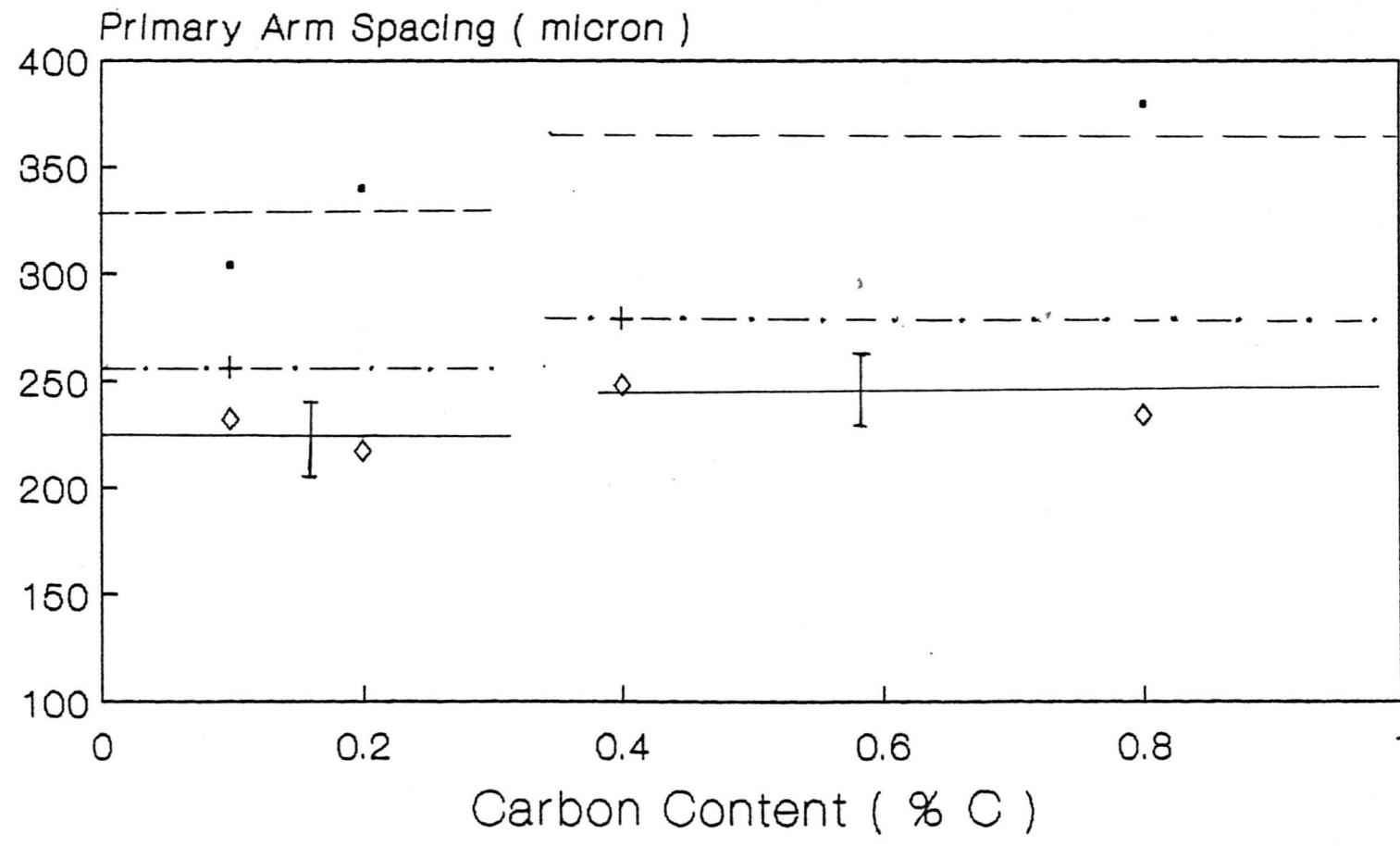
Figure 42

The effect of carbon content and temperature gradient on
primary arm spacing for different growth rates

a- 1.5 mm/min

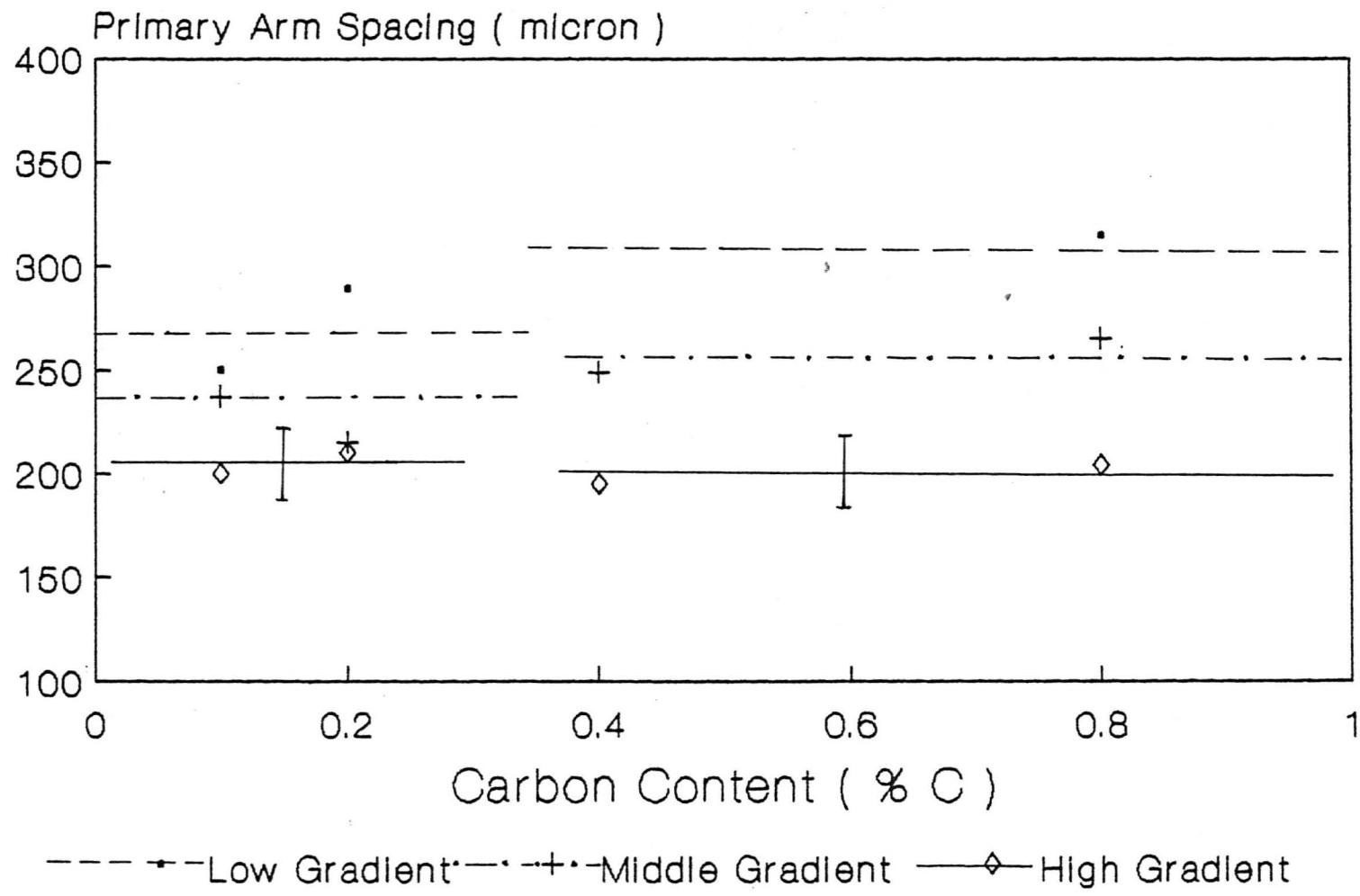
b- 6 mm/mm

c- 15 mm/min



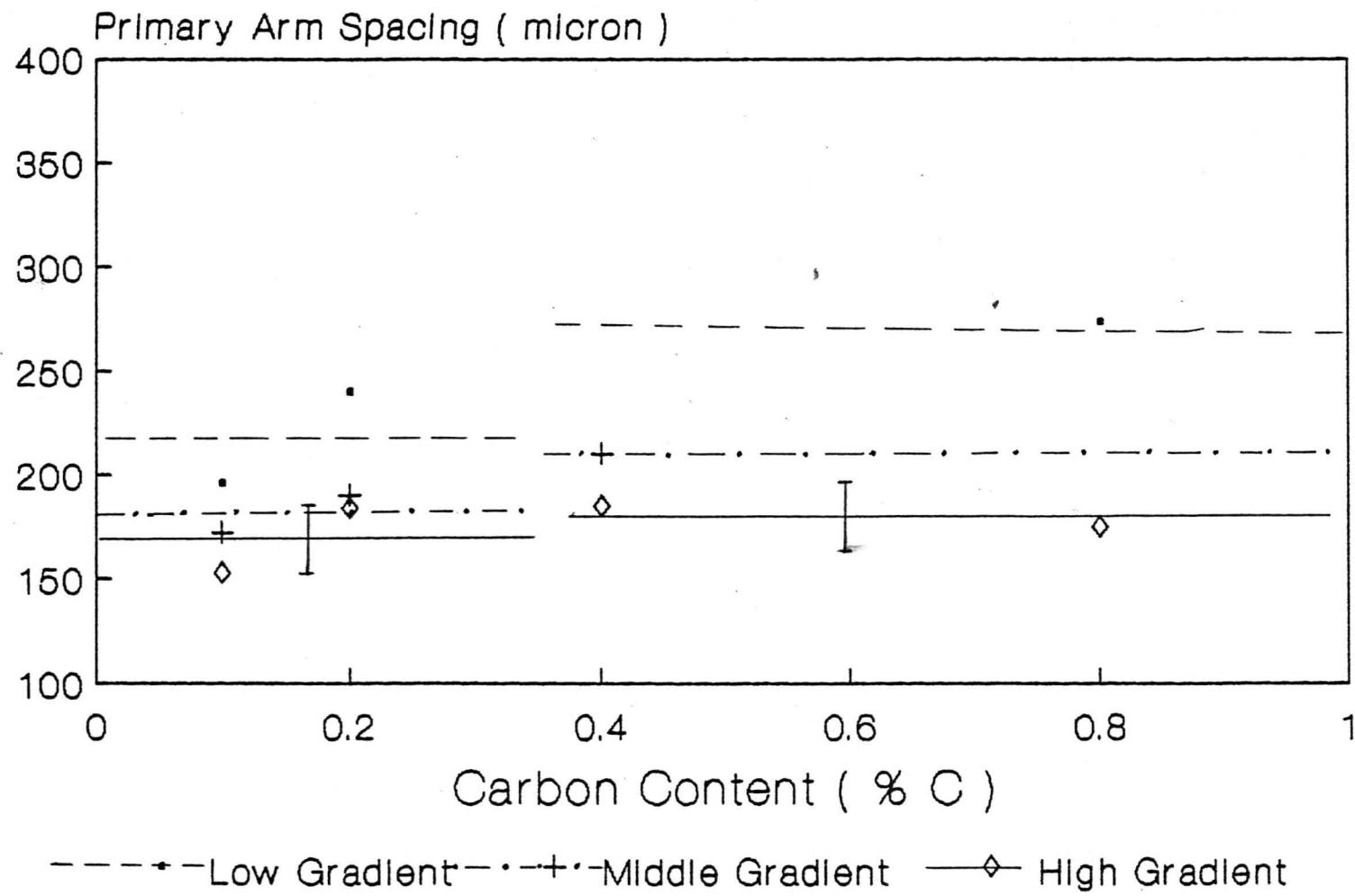
(a)

1.5 mm/min



6 mm/min

(b)

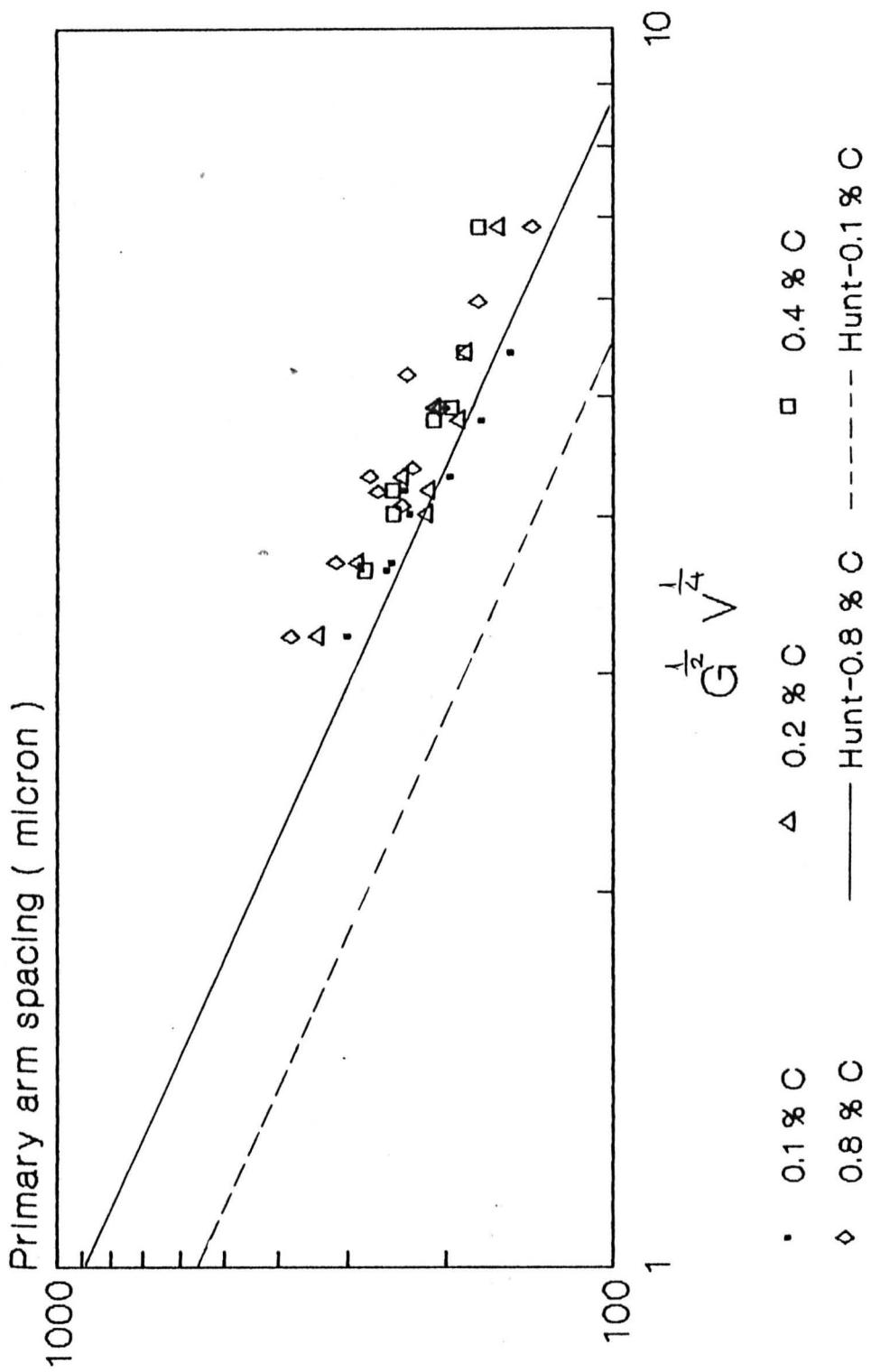


15 mm/min

(c)

Figure 43

**Comparison between Hunt equation prediction for 0.8 % C and
0.1 % C and present work data**



Figures 44 to 53

**Secondary arm spacing as a function of solidification time for
all carbon content and each power series**

- 44) 0.1 % C - 1 series**
- 45) 0.1 % C - 2 series**
- 46) 0.2 % C - 1 series**
- 47) 0.2 % C - 2 series**
- 48) 0.2 % C - 3 series**
- 49) 0.4 % C - 2 series**
- 50) 0.4 % C - 3 series**
- 51) 0.8 % C - 1 series**
- 52) 0.8 % C - 2 series**
- 53) 0.8 % C - 3 series**

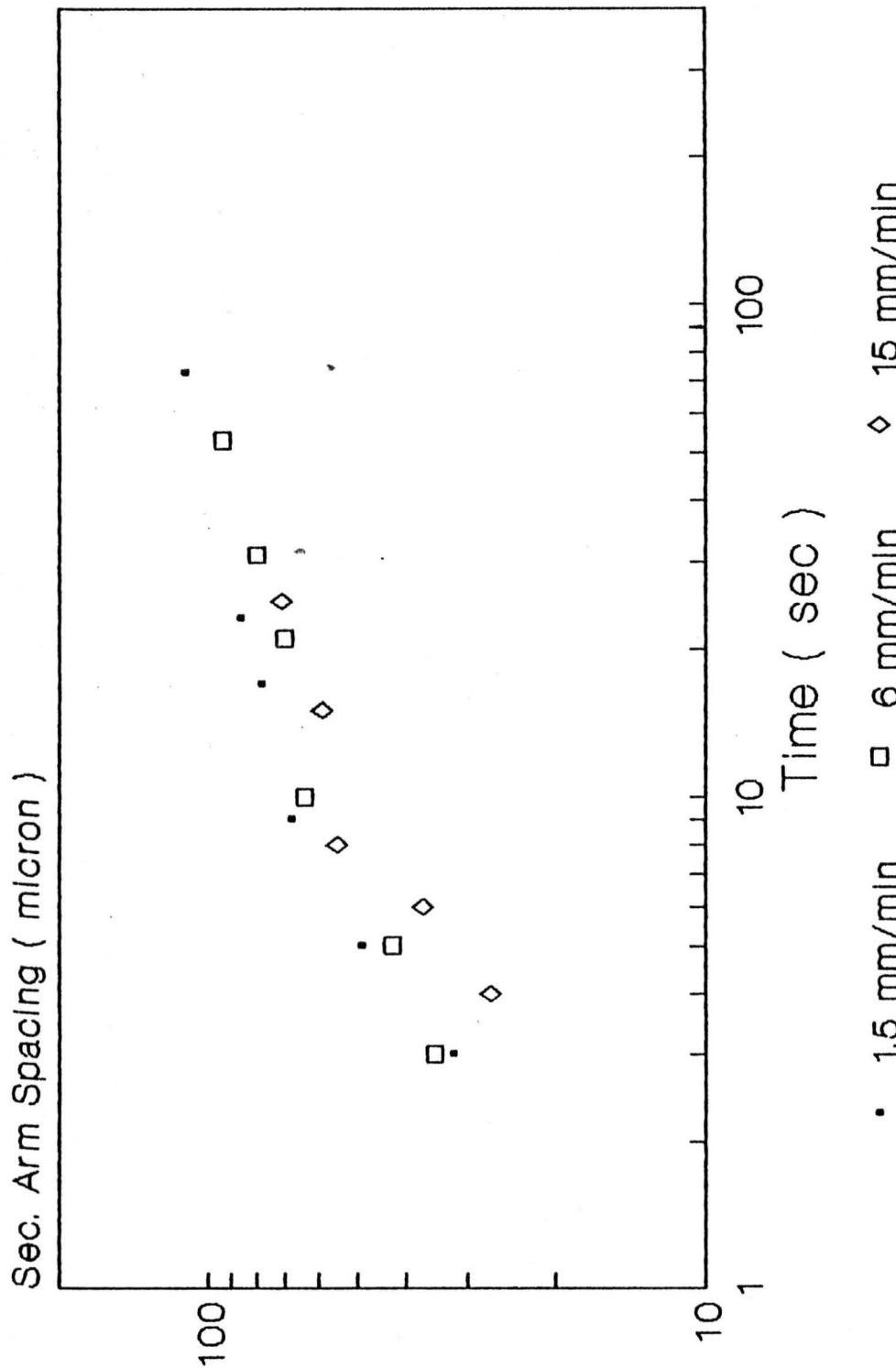


Figure 44

Sec. Arm Spacing (micron)

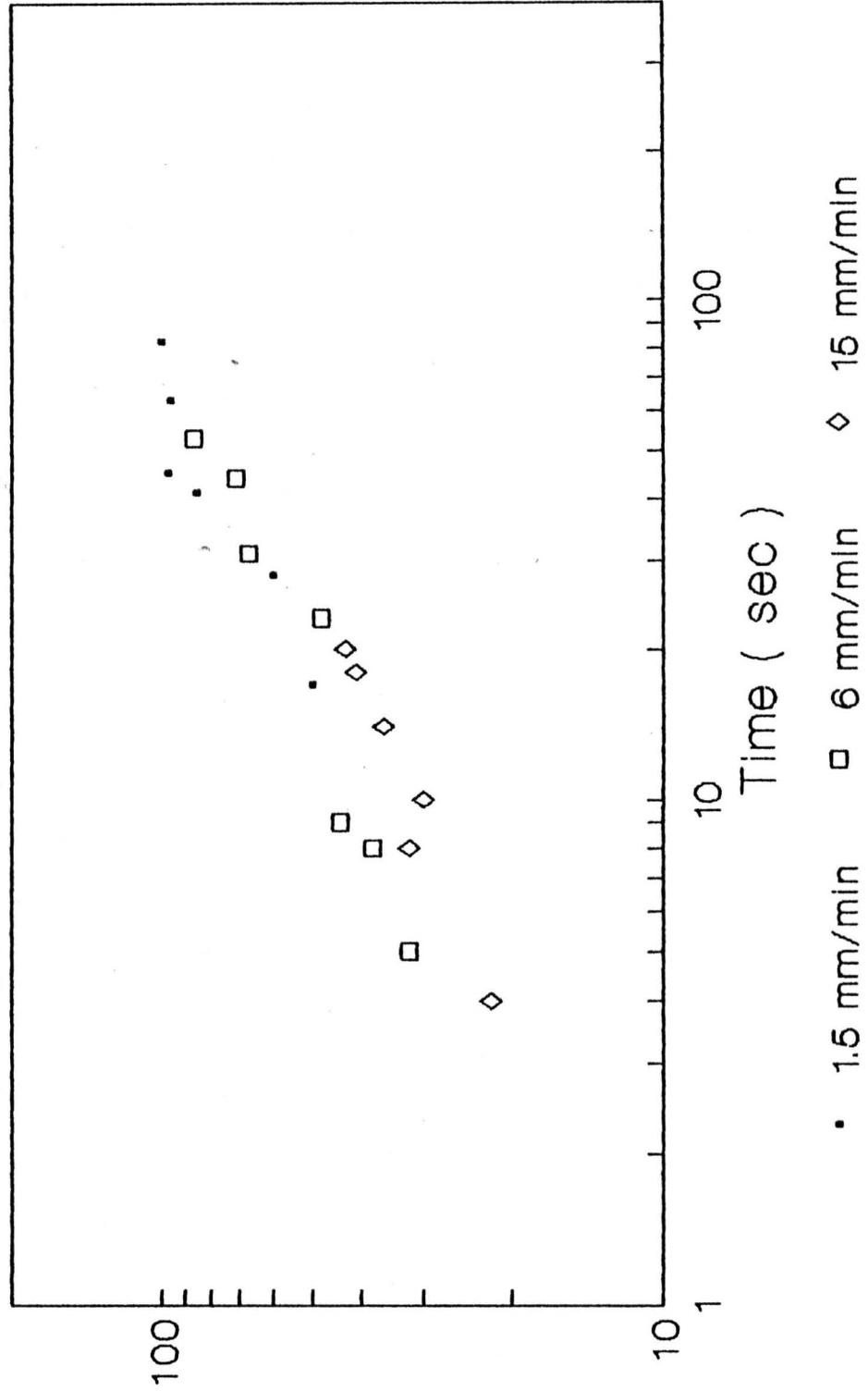


Figure 45

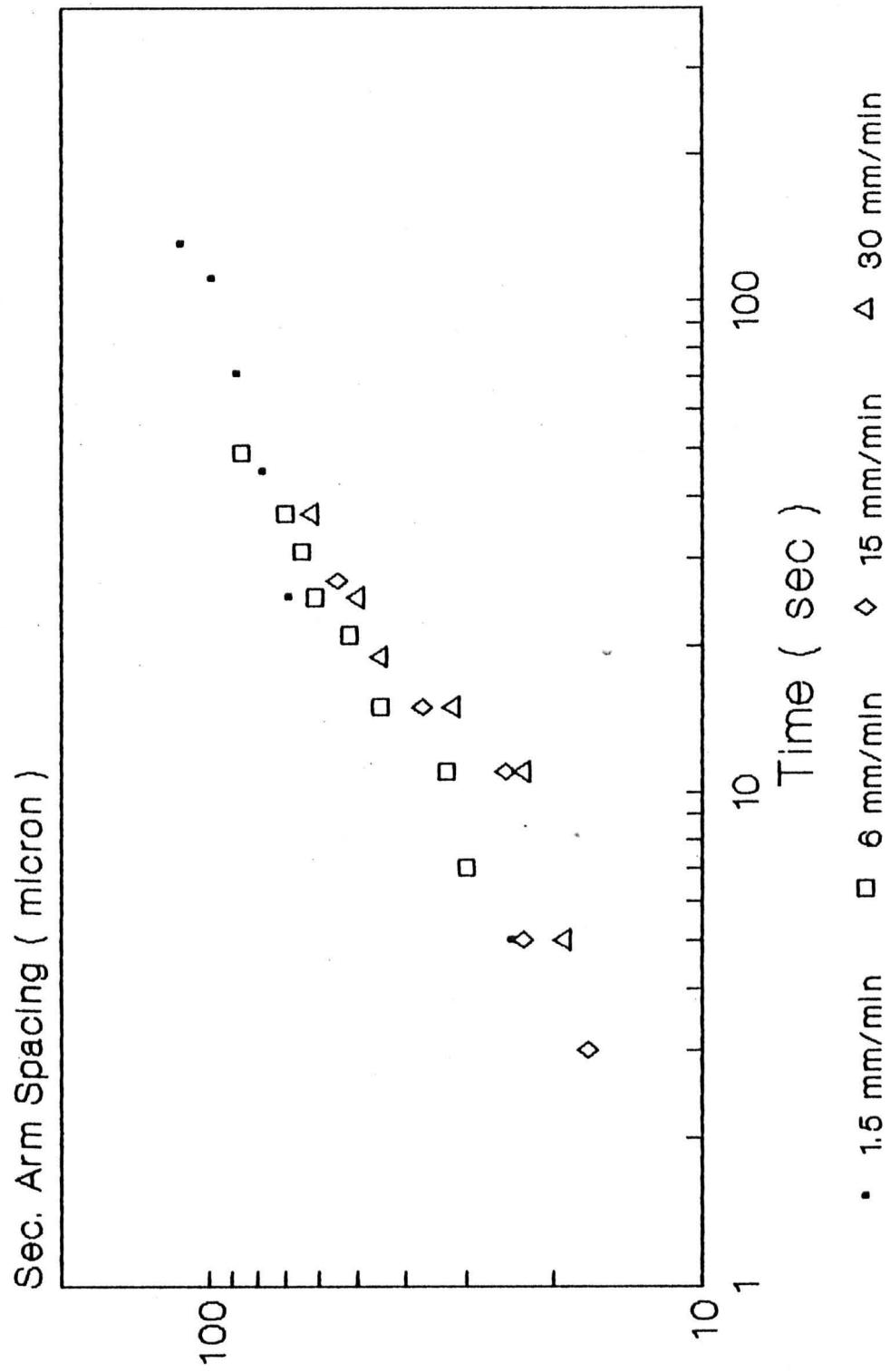


Figure 46

Sec. Arm Spacing (micron)

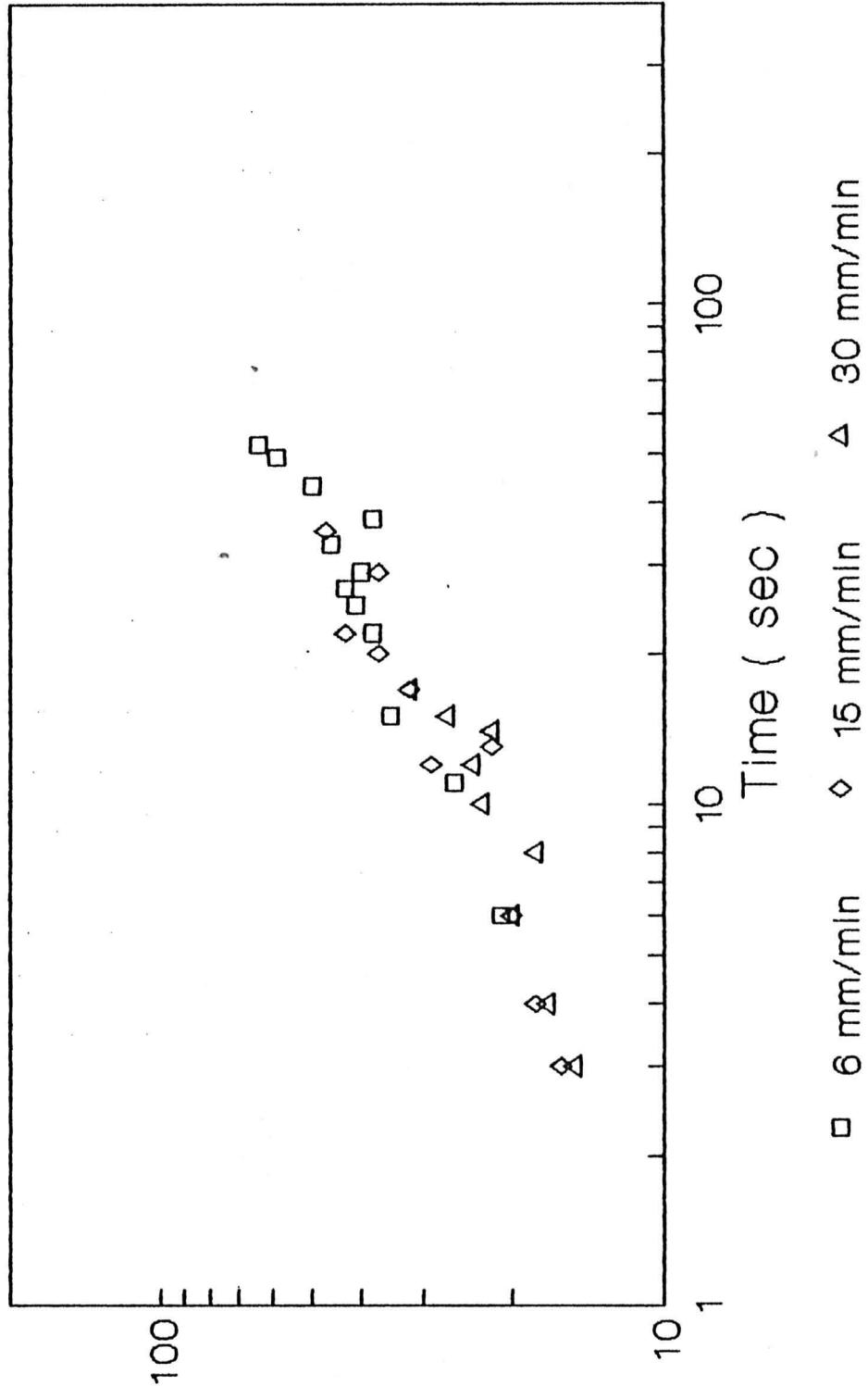


Figure 47

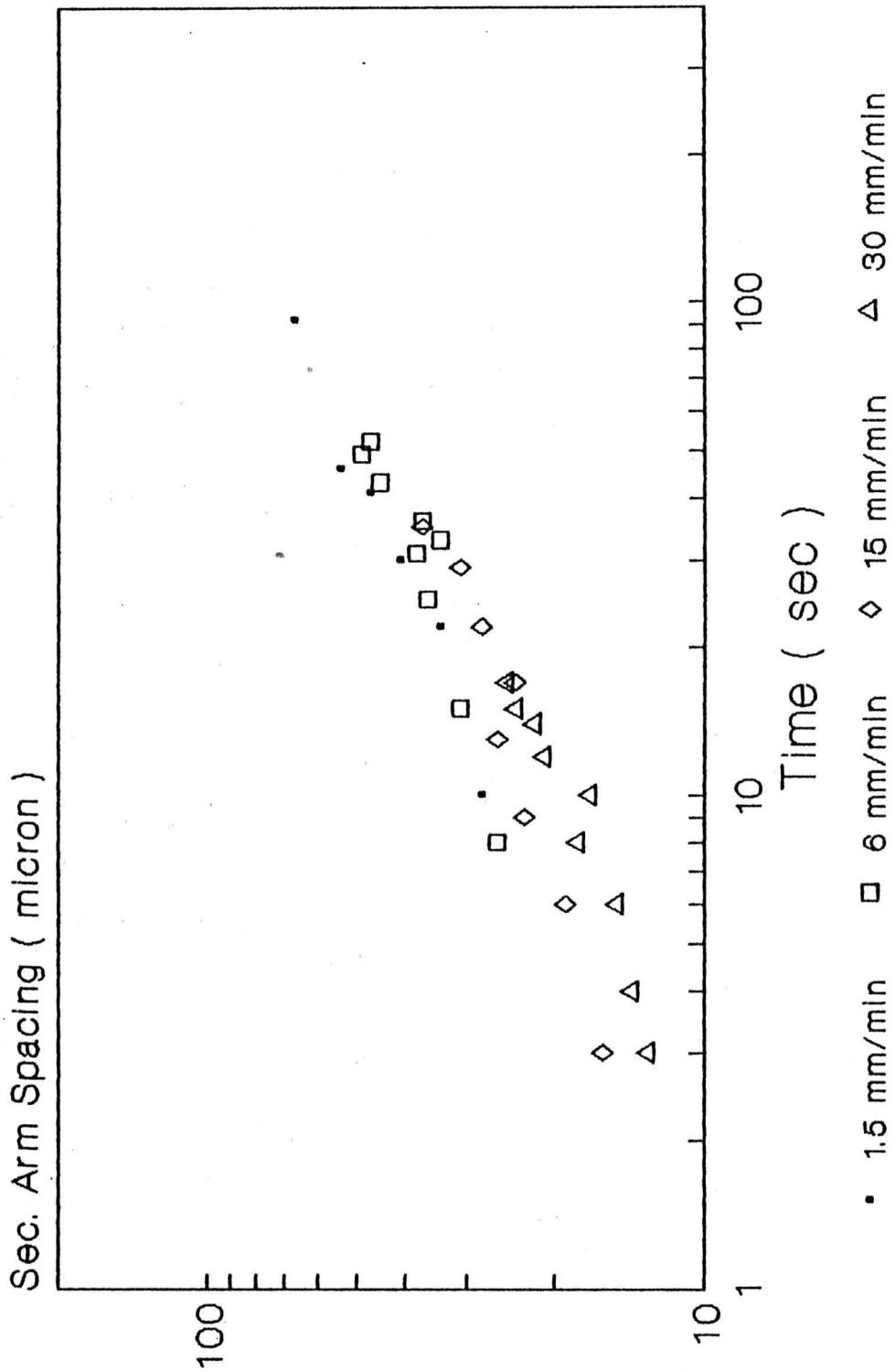


Figure 48

Sec. Arm Spacing (micron)

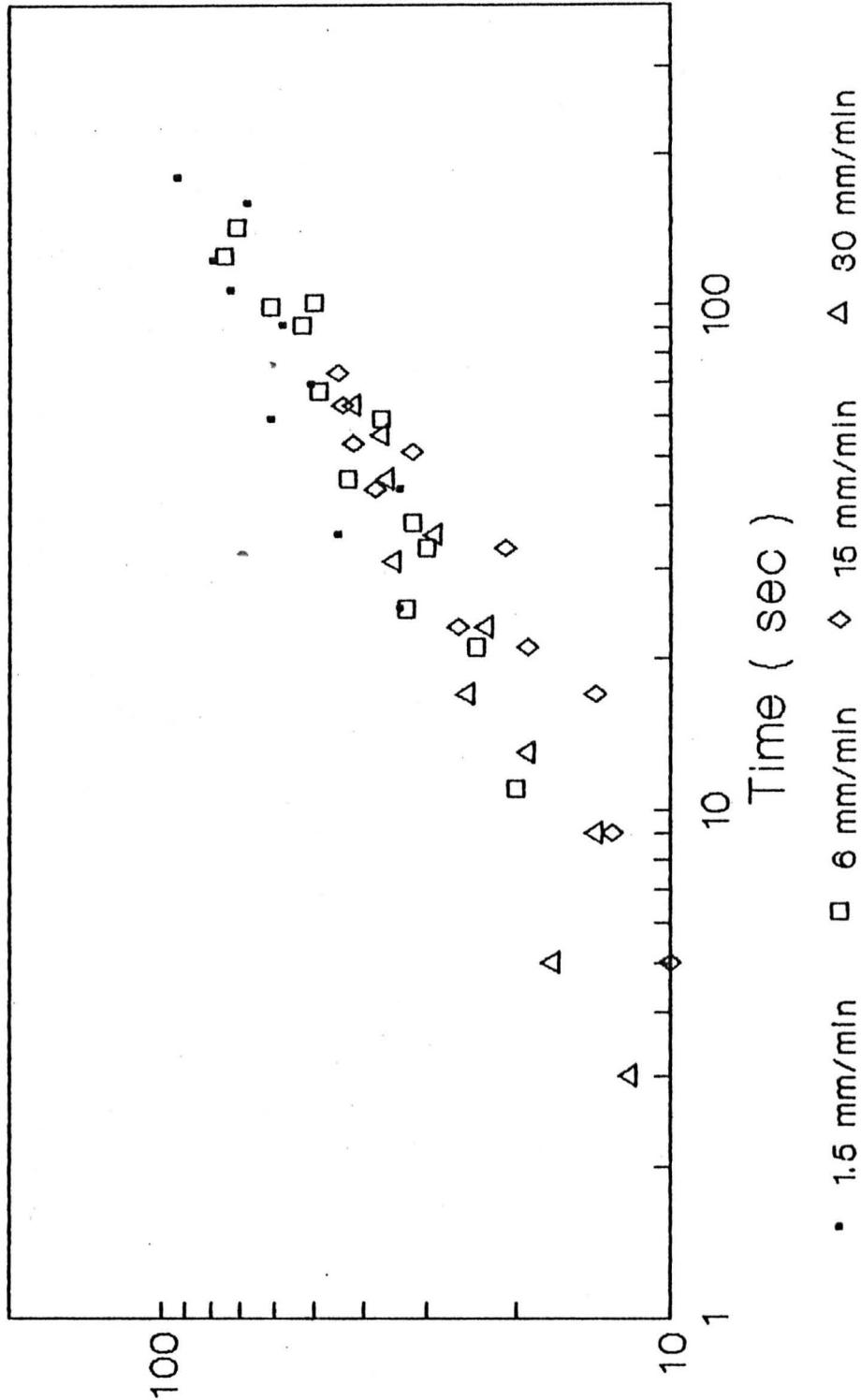


Figure 49

Sec. Arm Spacing (micron)

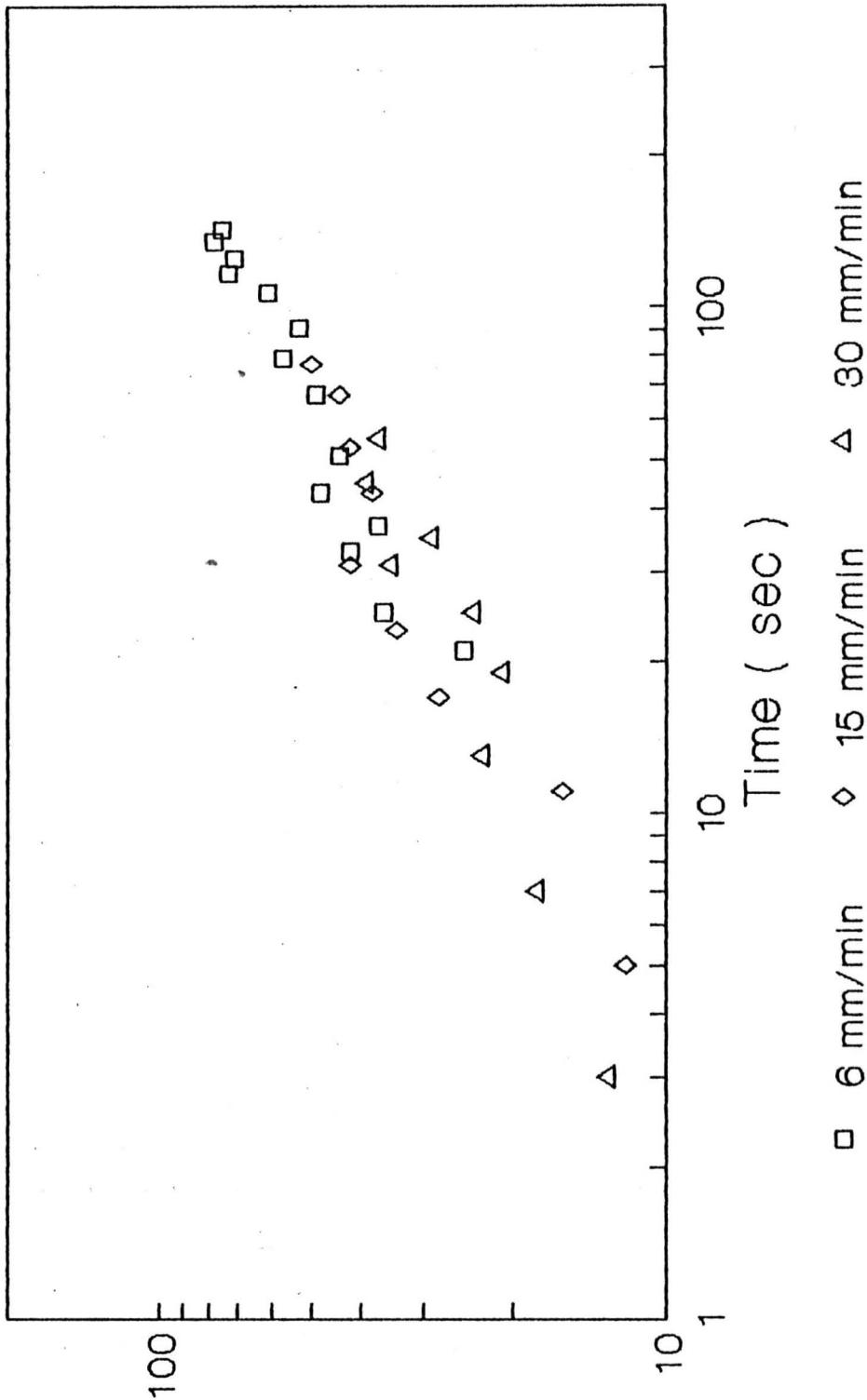


Figure 50

Sec. Arm Spacing (micron)

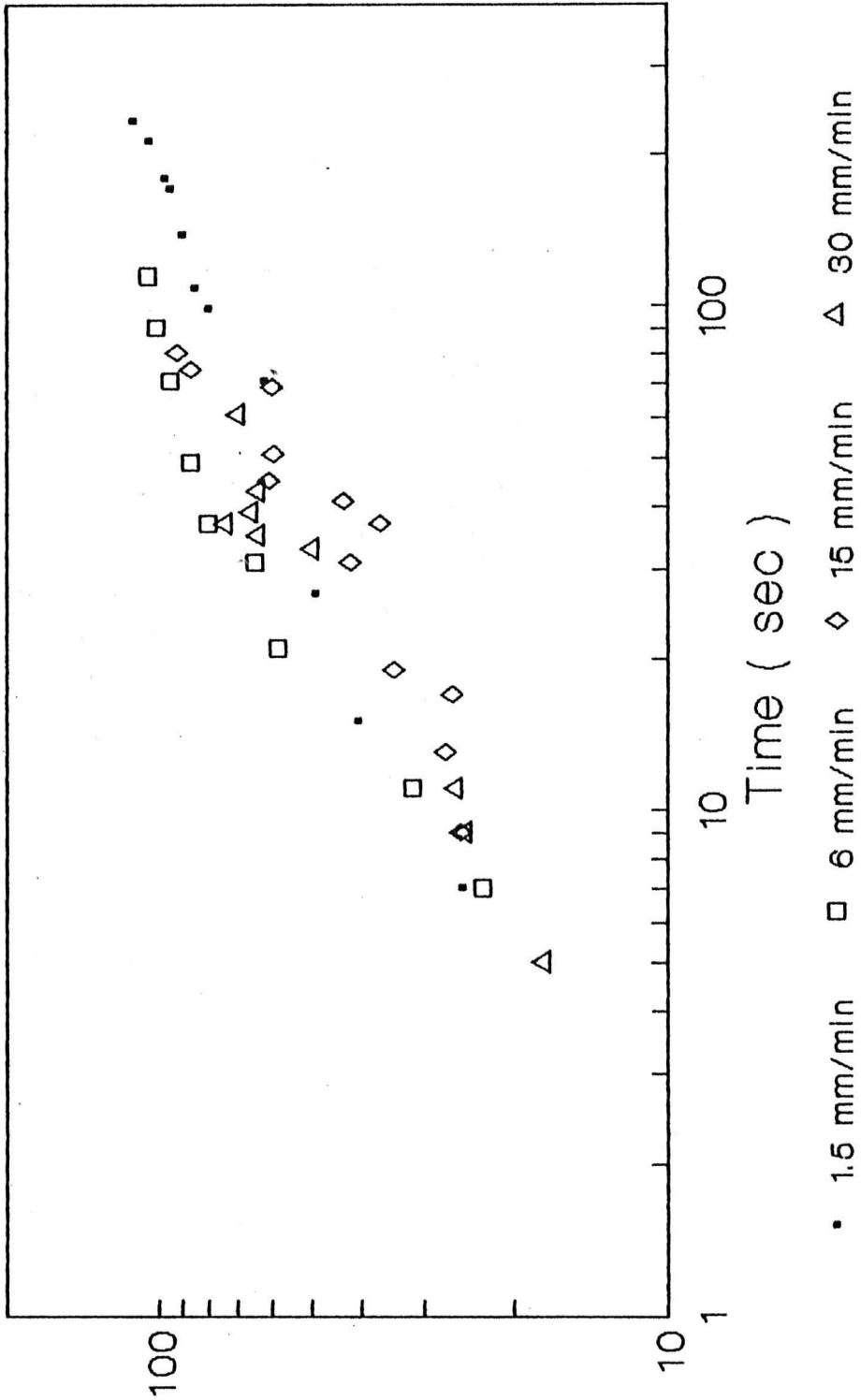


Figure 51

Sec. Arm Spacing (micron)

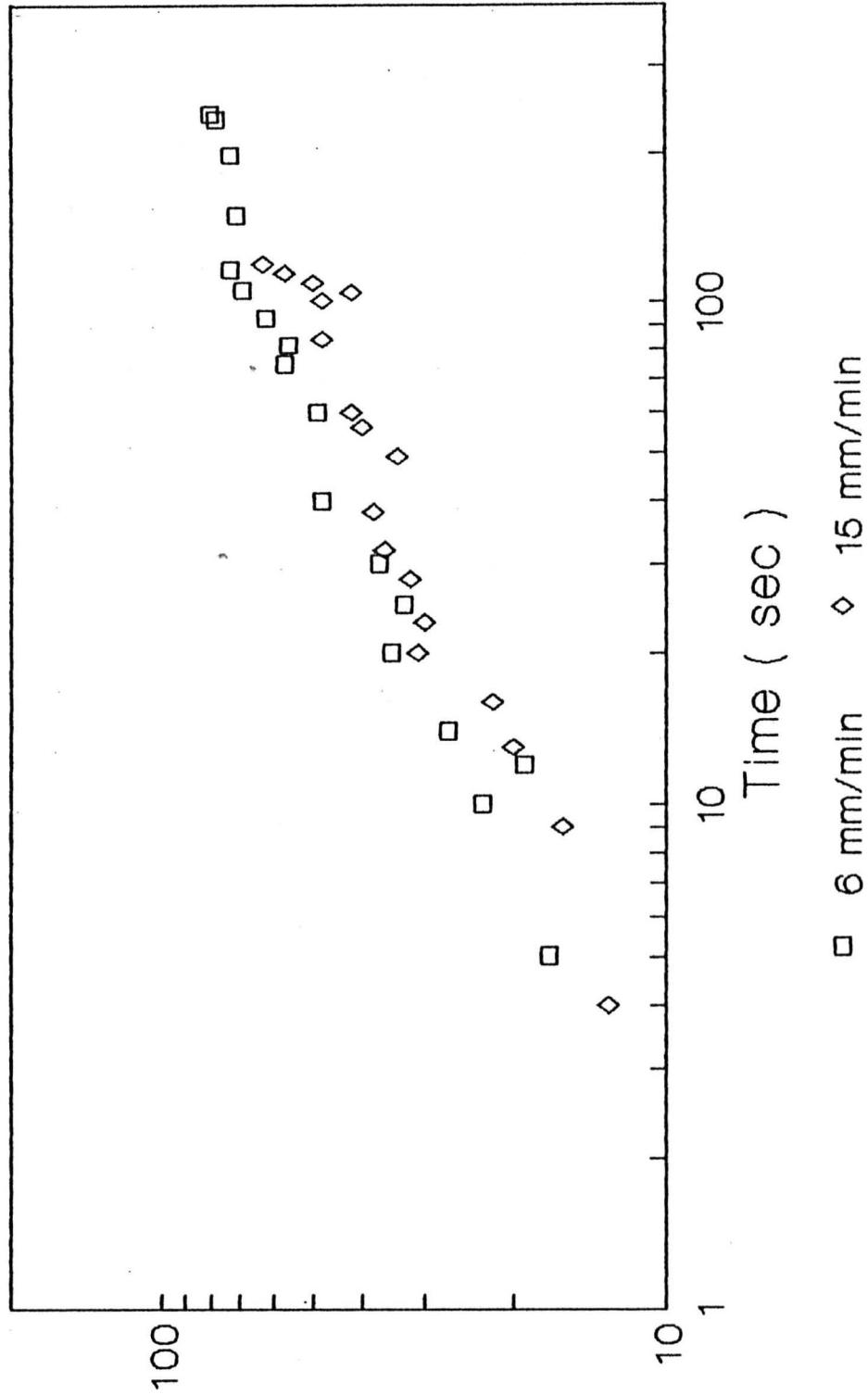


Figure 52

Sec. Arm Spacing (micron)

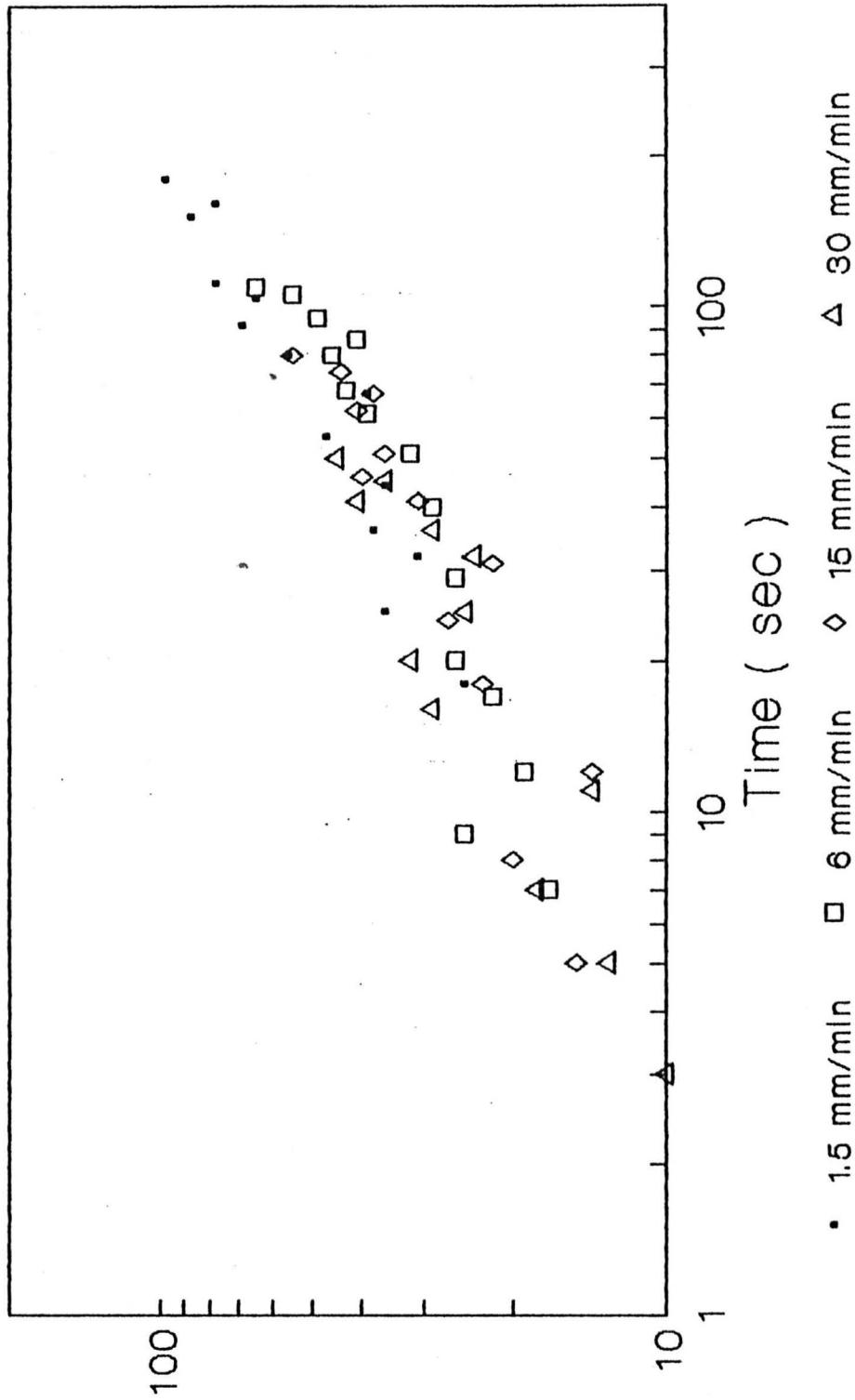


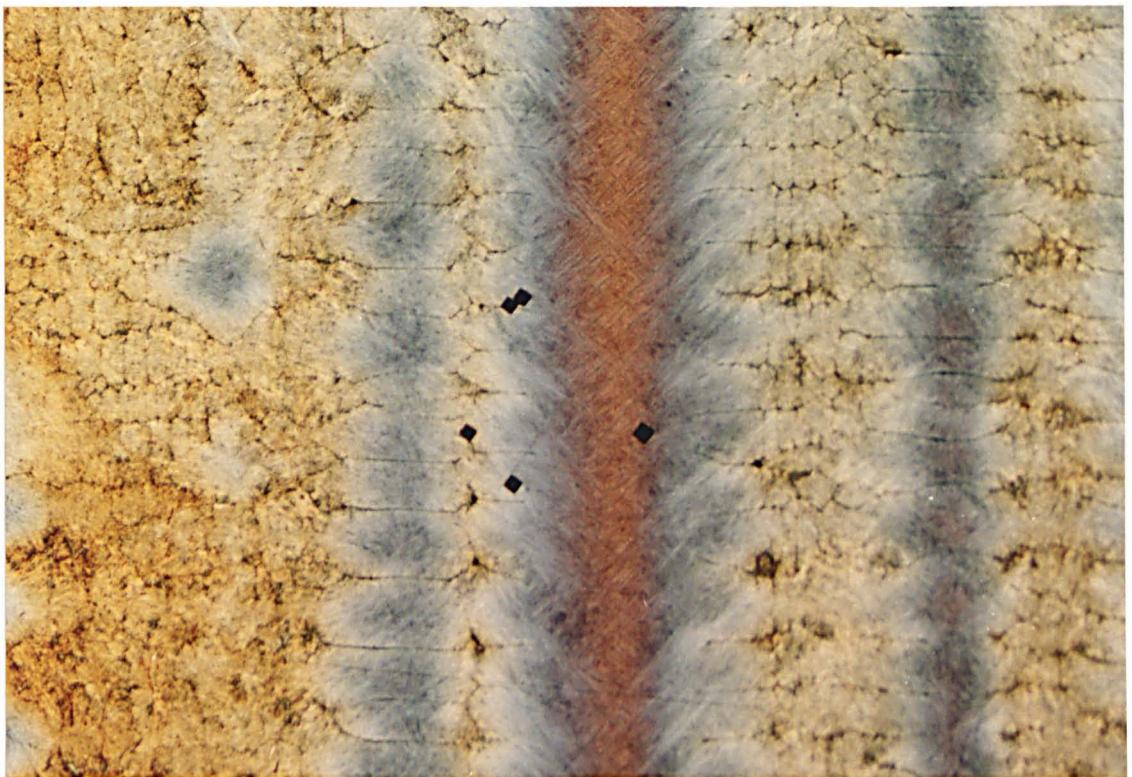
Figure 53

Figure 54

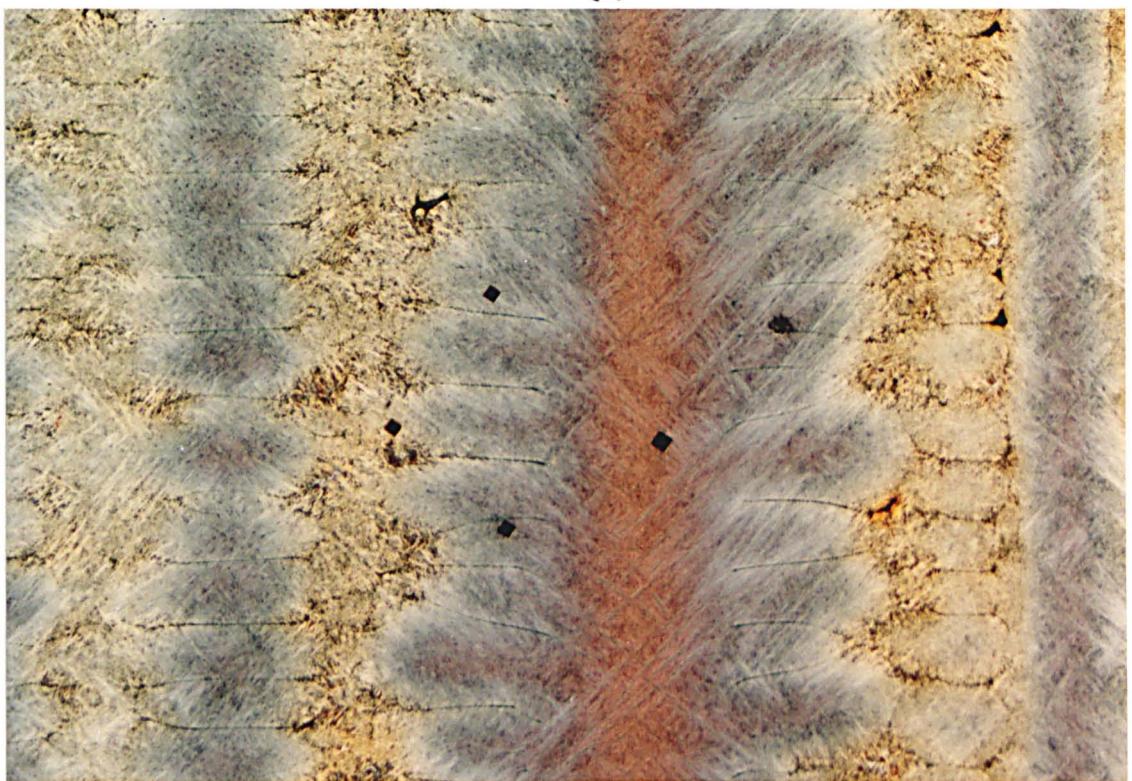
Typical longitudinal sections of secondary arms. Hardness indentation show the chosen electron micro-probe analyse lines through and perpendicular to the secondary arms

0.8 % C - 1.6 % Mn - Fe

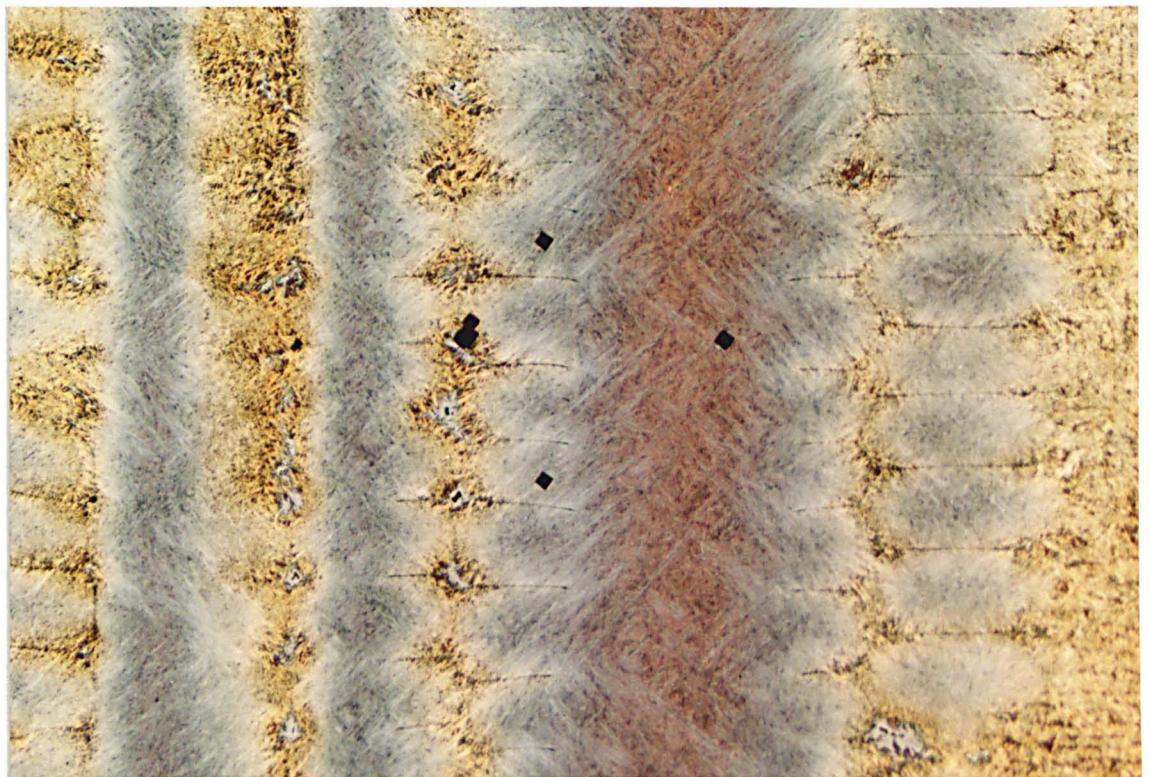
Magnification	51.3
a-	0.9 mm behind tips
b-	2 mm behind tips
c-	3.8 mm behind tips
d-	6 mm behind tips
e-	26 mm behind tips



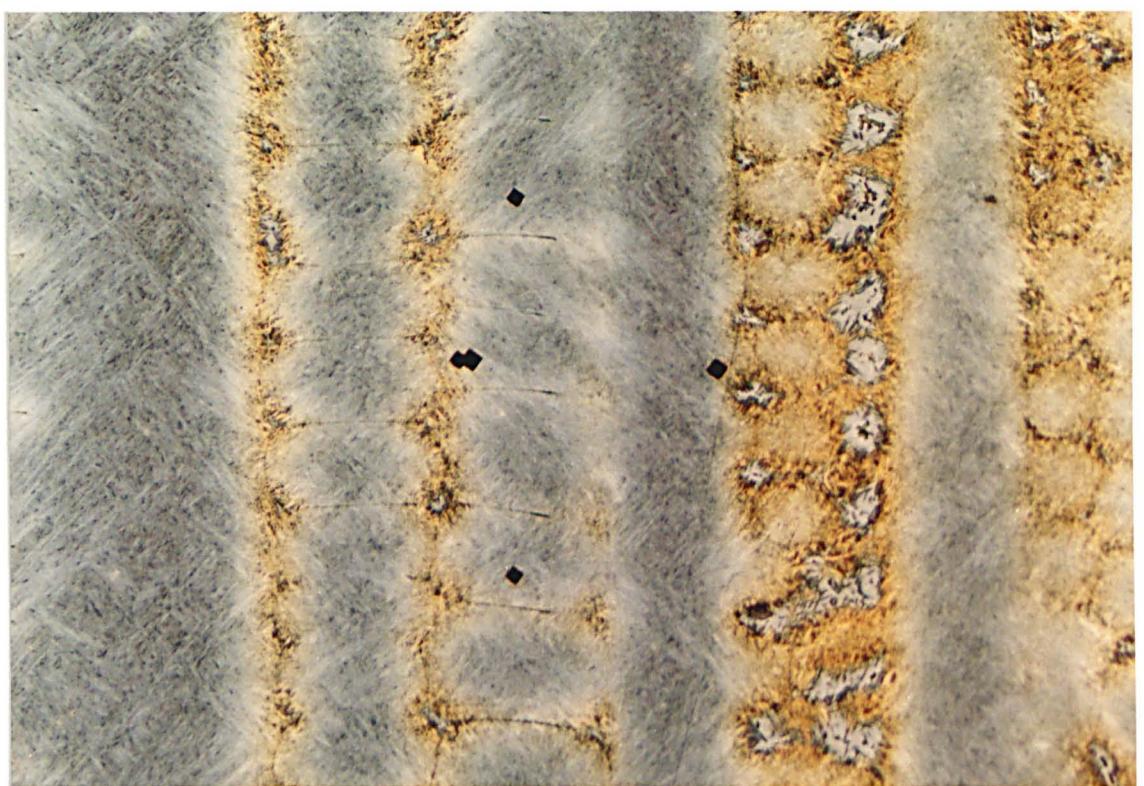
(a)



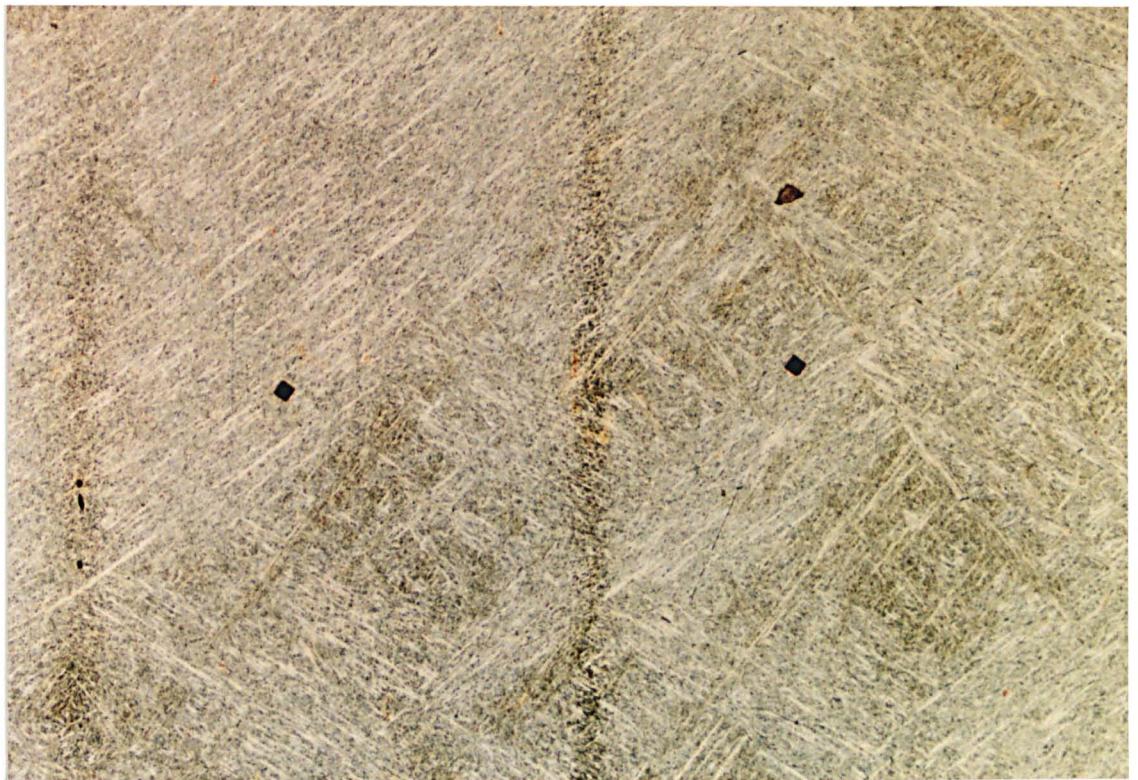
(b)



(c)



(d)



(e)

Figure 55

The change of C_{min} as a function of temperature below liquidus
and growth rate for 0.1 % C - 1.6 % Mn - Fe alloy

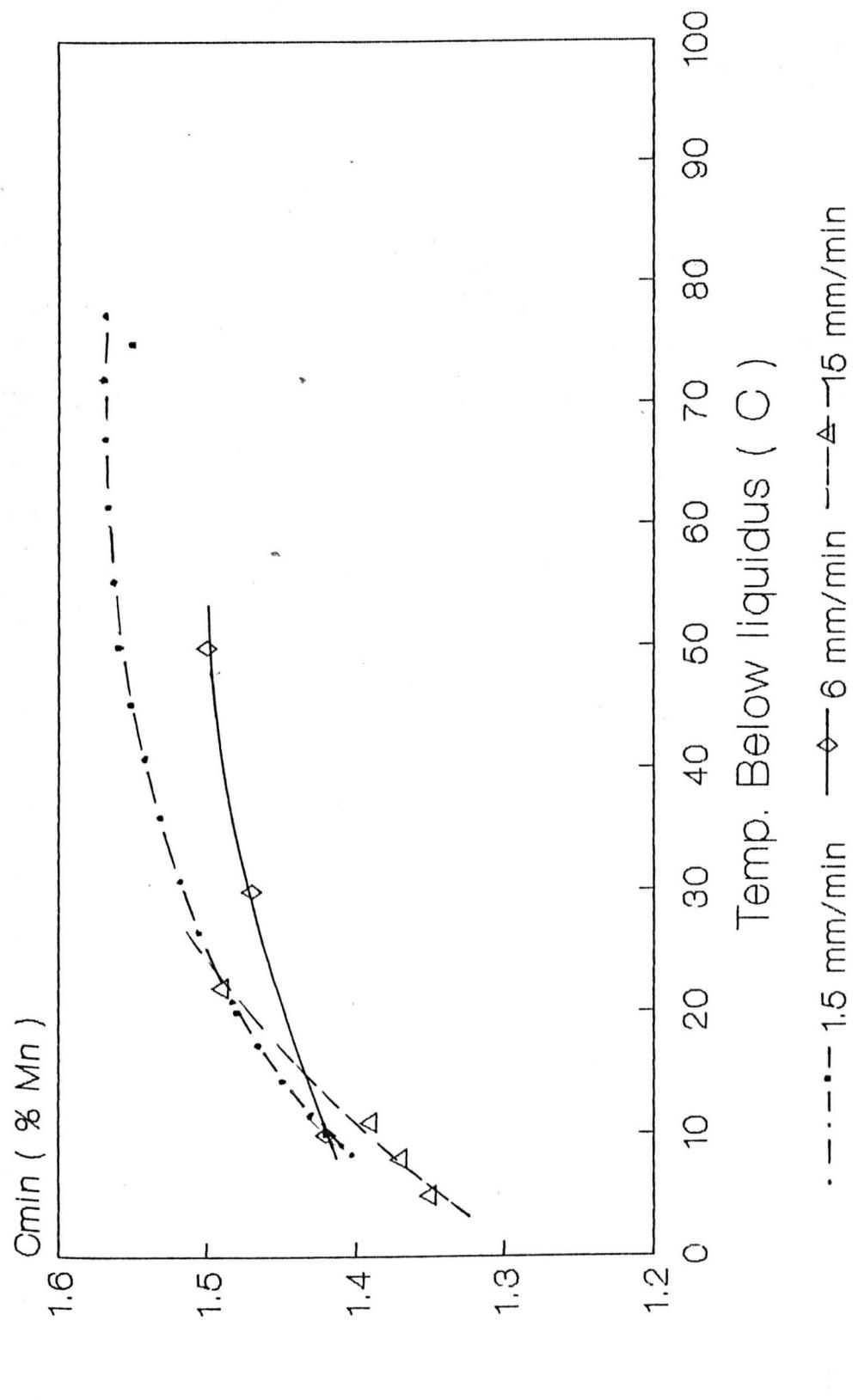


Figure 56

**The change in C_{min} as a function of temperature below liquidus
and growth rate for 0.2 % C - 1.6 % Mn - Fe alloy**

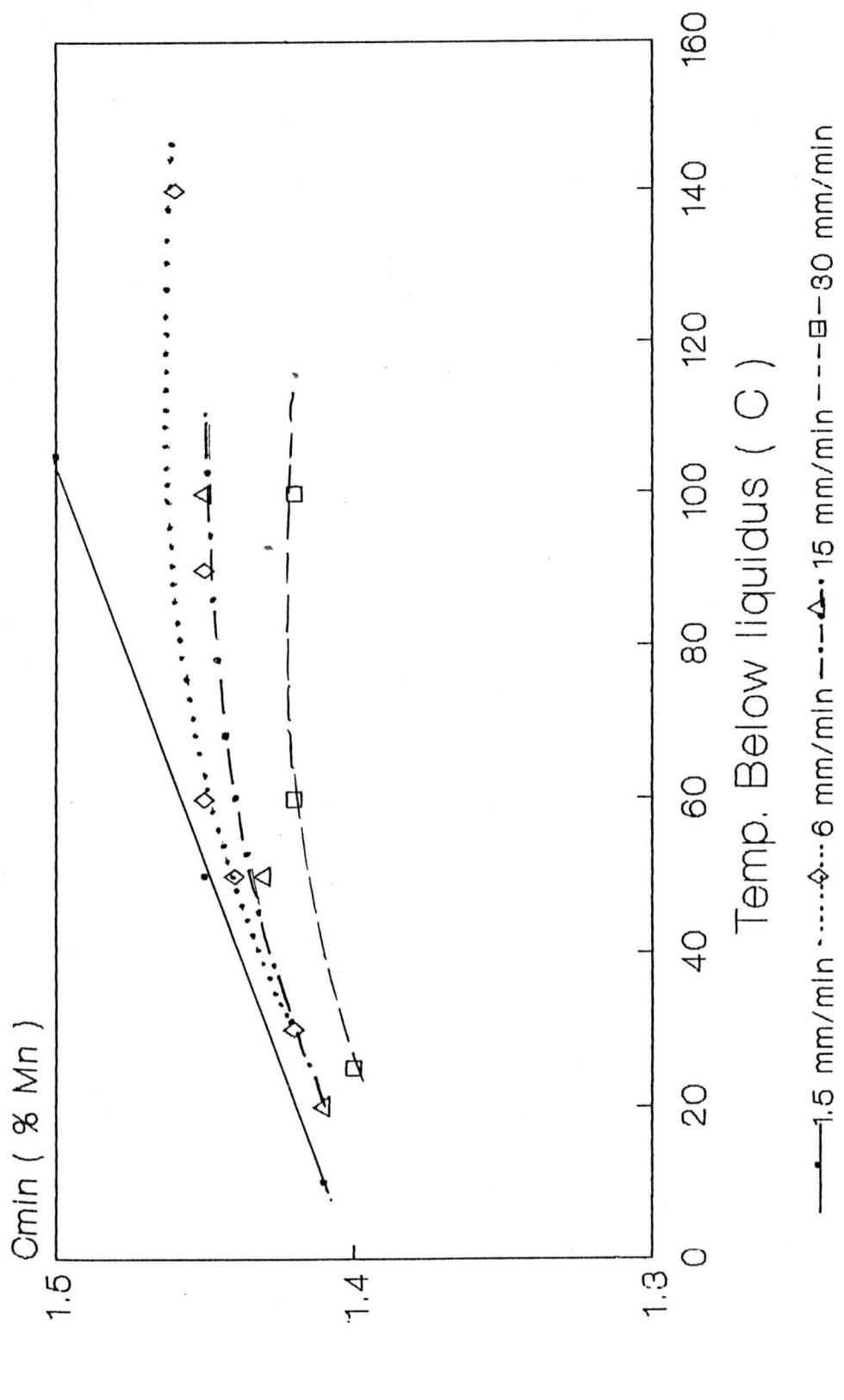


Figure 57

The change of C_{min} as a function of temperature below liquidus
and gradient in liquid for 0.2 % C - 1.6 % Mn - Fe alloy at
30 mm/min

Low Gradient	3.5 C/mm
Middle Gradient	4.6 C/mm
High Gradient	6.9 C/mm

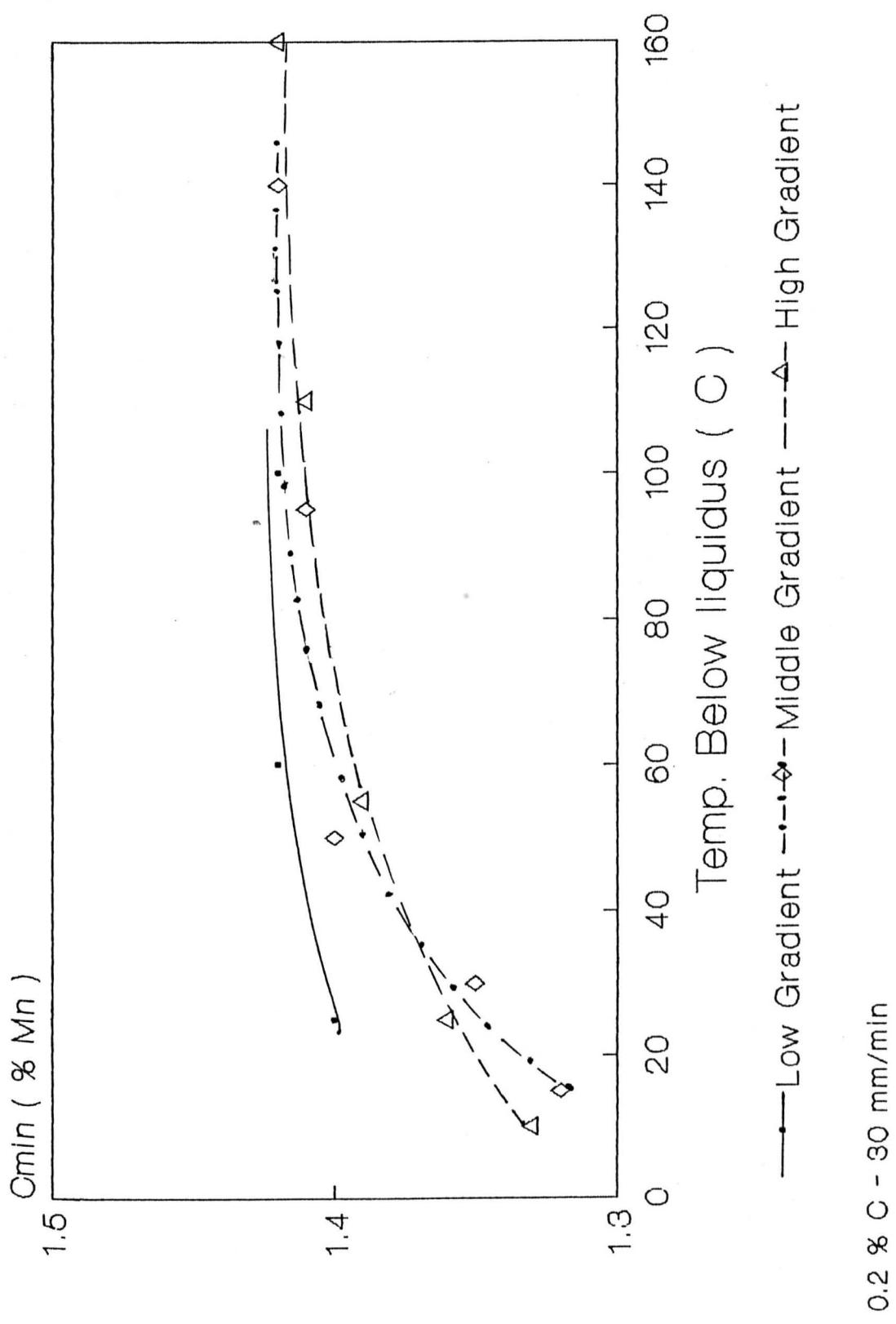
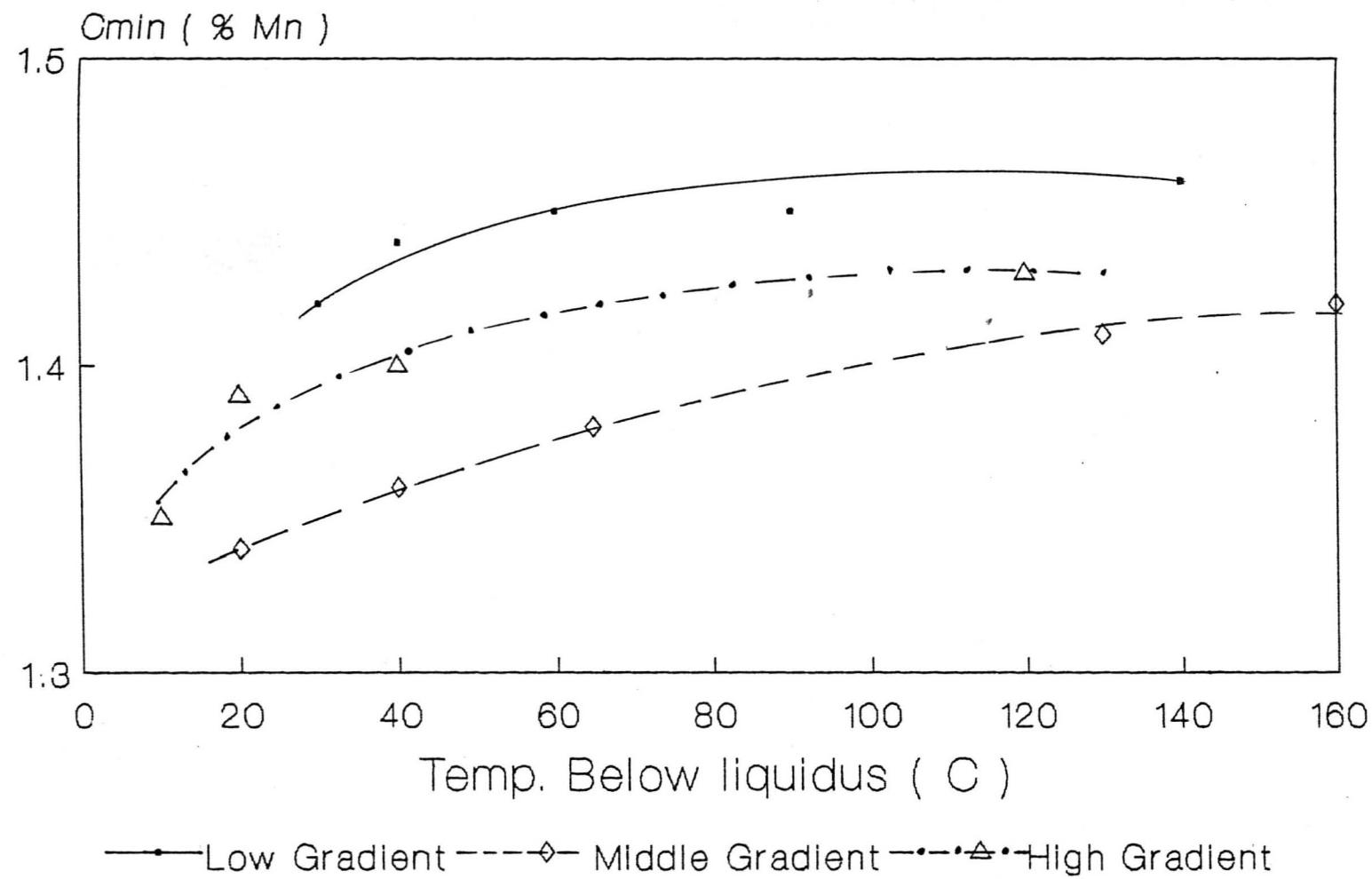


Figure 58

The change of C_{min} as a function of temperature below liquidus and gradient in liquid for 0.2 % C - 1.6 % Mn - Fe alloy at 6 mm/min

Low Gradient	5.5 C/mm
Middle Gradient	7.2 C/mm
High Gradient	9.8 C/mm



0.2 % C - 6 mm/min

Figure 59

The change of C_{min} as a function of temperature below liquidus
and growth rate for 0.4 % C - 1.6 % Mn - Fe alloy

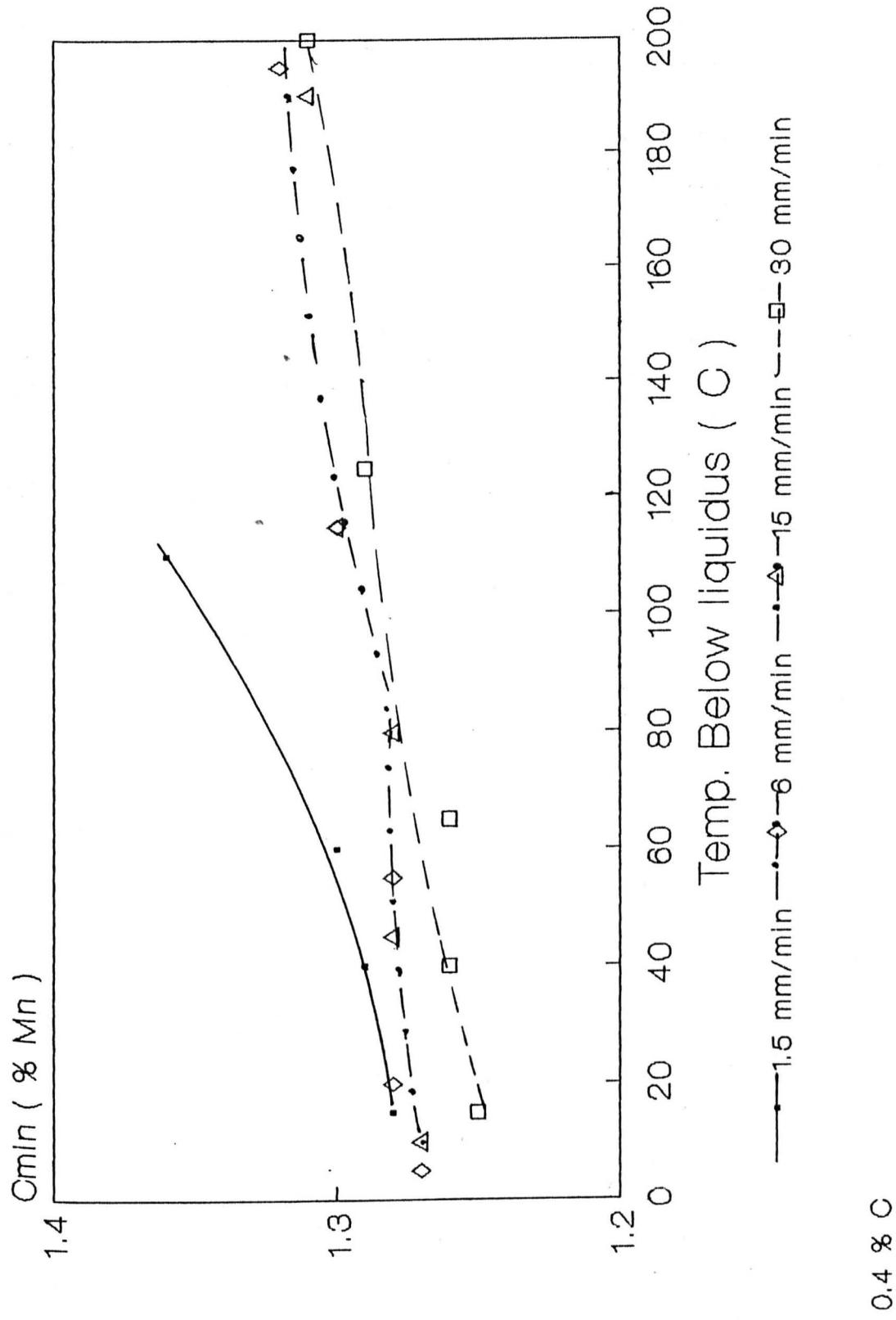


Figure 60

The change of C_{min} as a function of temperature below liquidus
and growth for 0.8 % C - 1.6 % Mn - Fe alloy

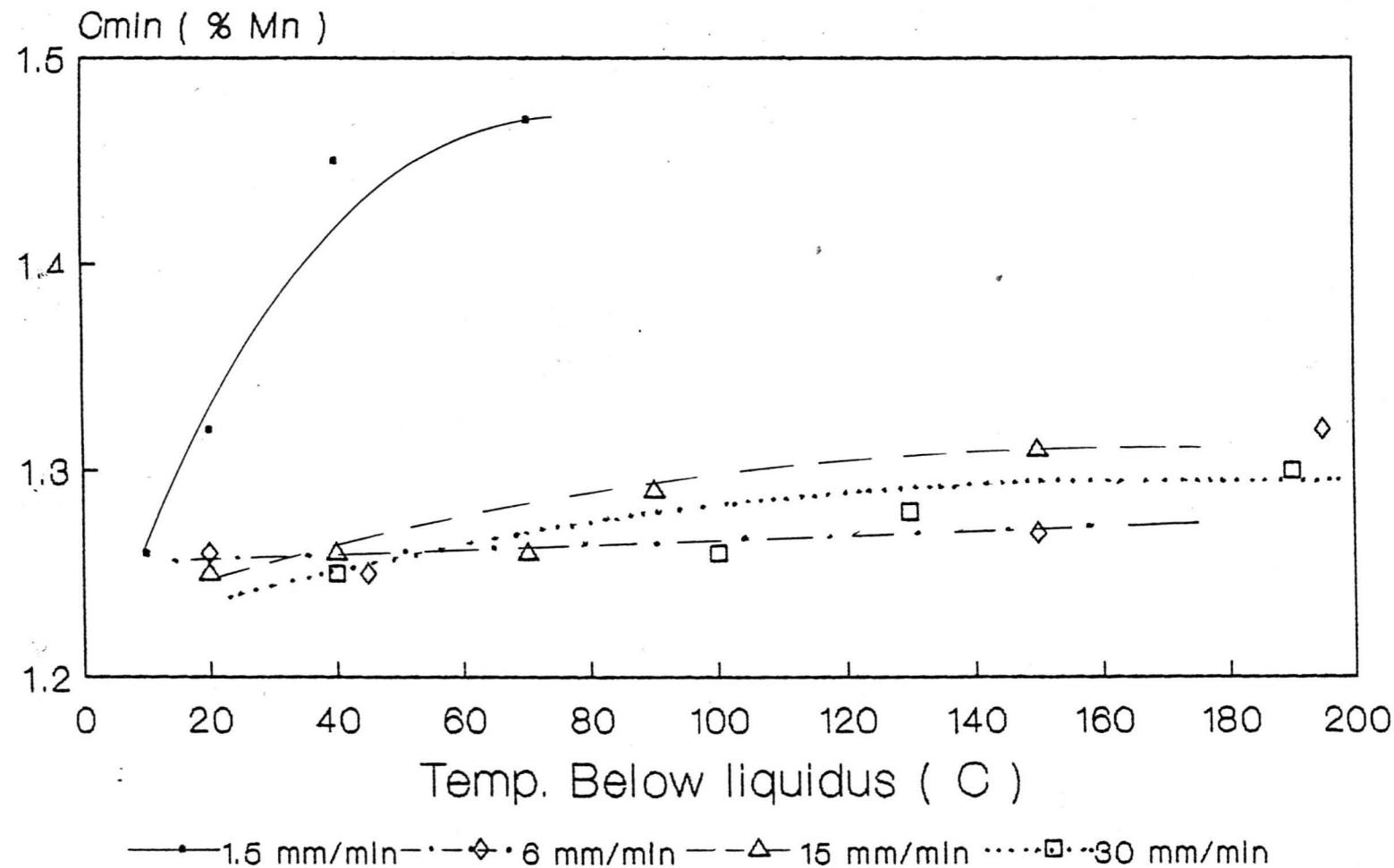


Figure 61

The change of C_{min} as a function of temperature below liquidus
and gradient in liquid for 0.4 % C - 1.6 % Mn - Fe alloy at
6 mm/min

Middle Gradient	7.2 C/mm
High Gradient	9.8 C/mm

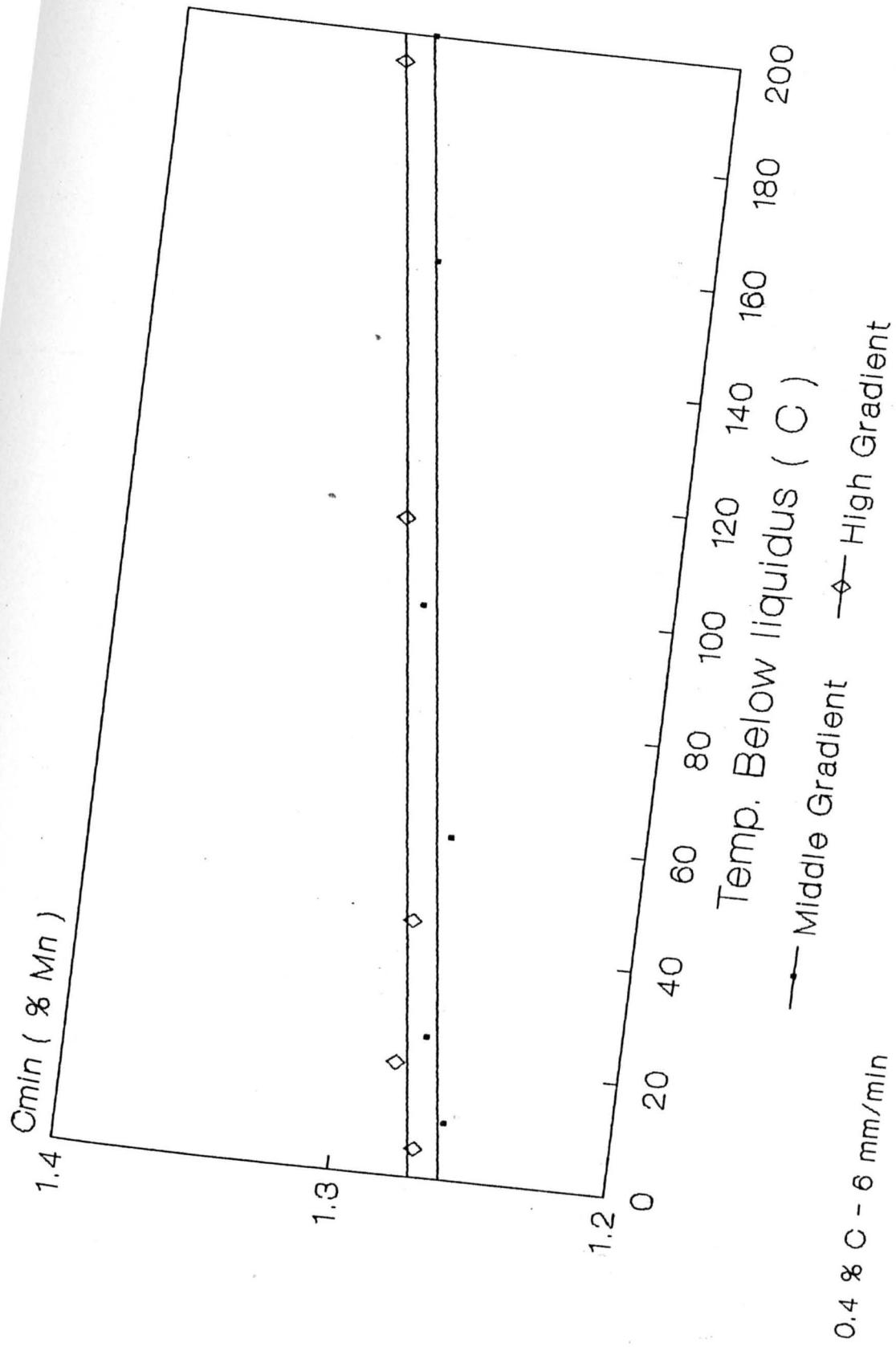
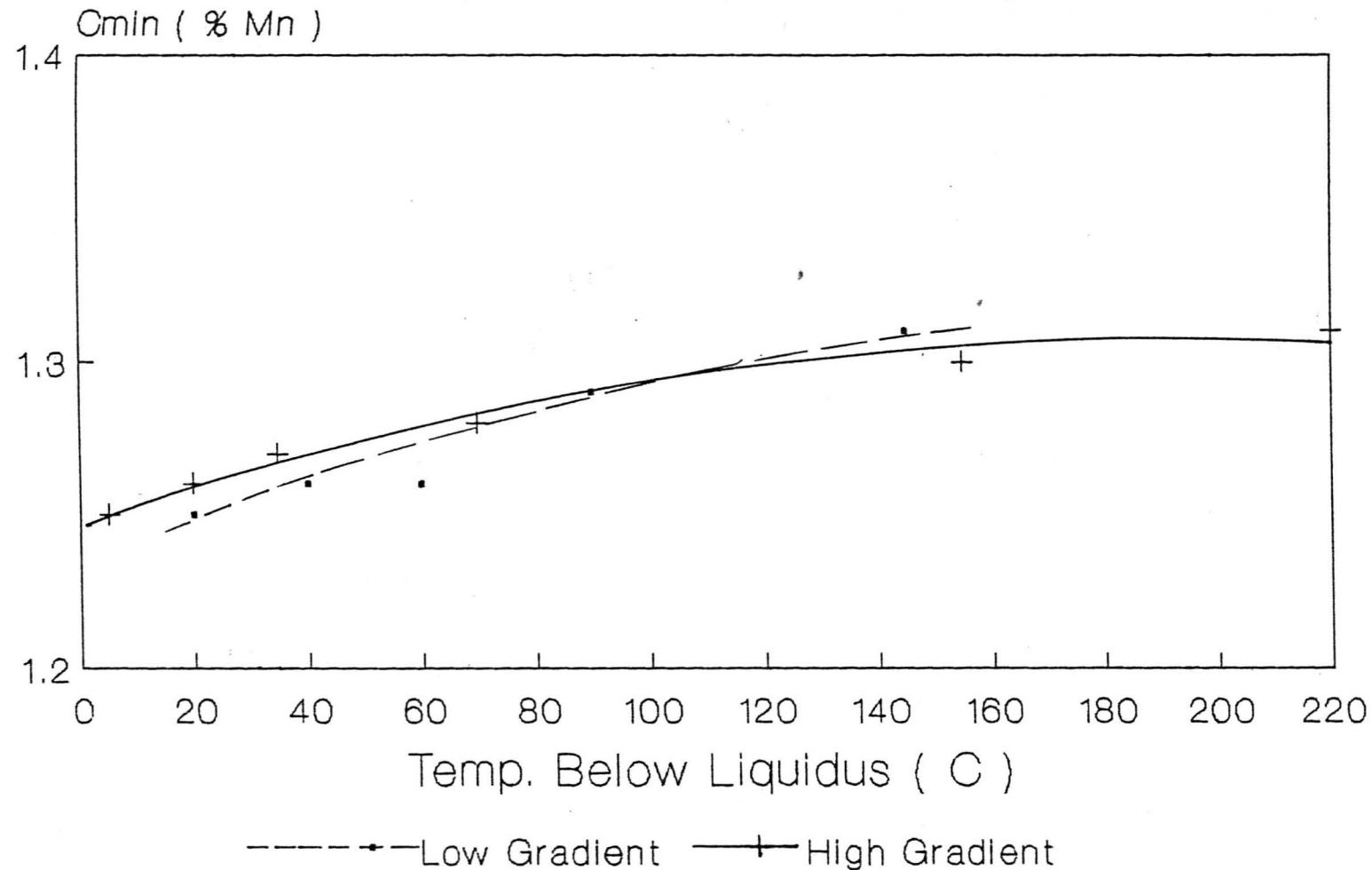


Figure 62

The change of C_{min} as a function of temperature below liquidus
and gradient in liquid for 0.8 % C - 1.6 % Mn - Fe alloy at
15 mm/min

Low Gradient 4.8 C/mm

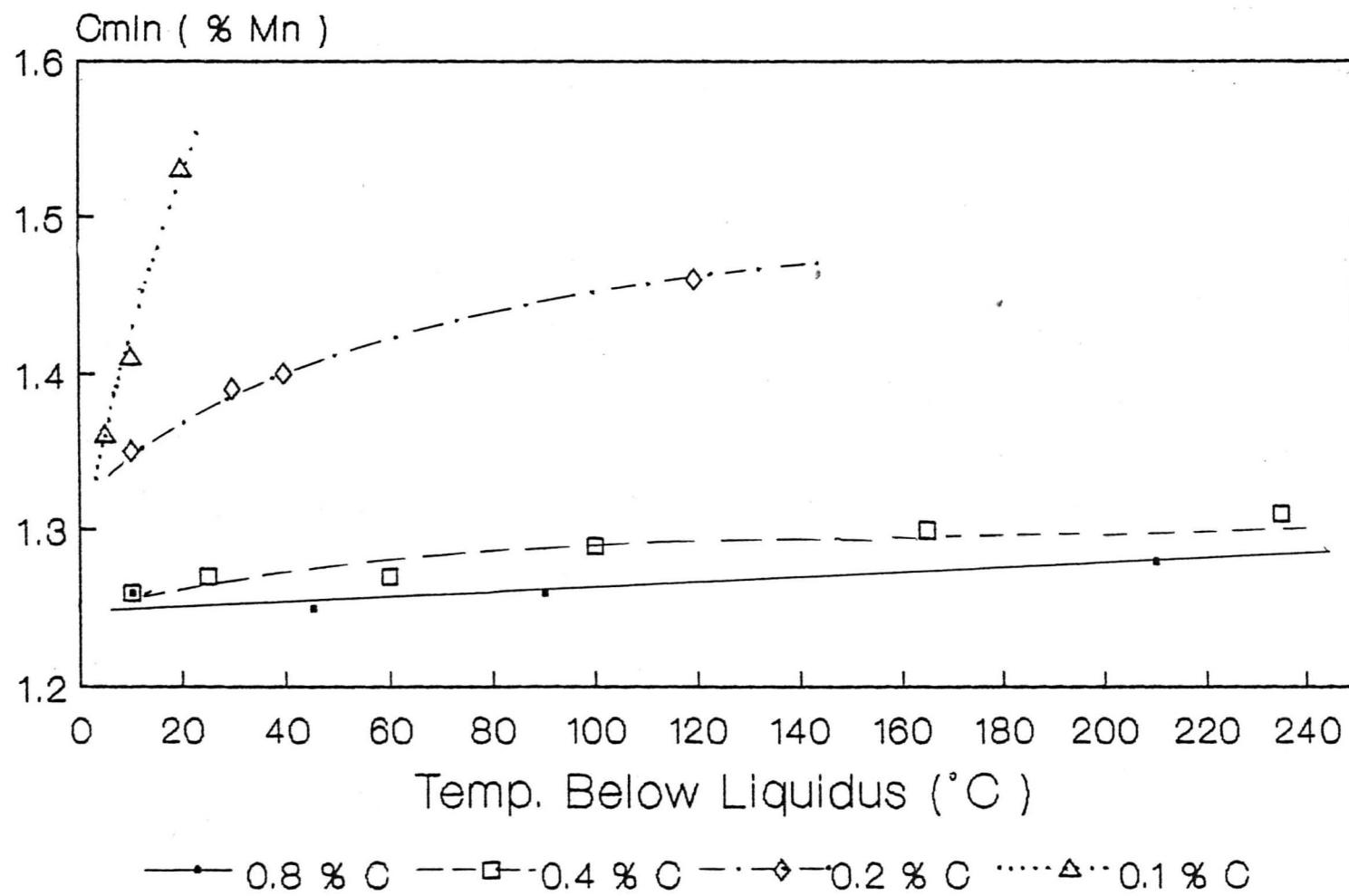
High Gradient 7.6 C/mm



0.8 % C - 15 mm/min

Figure 63

The change of C_{min} as a function of temperature below liquidus
and carbon content at 6 mm/min under 9.8 C/mm in liquid



6 mm/min

Figure 64

The change in Cmax between secondary arms during growth

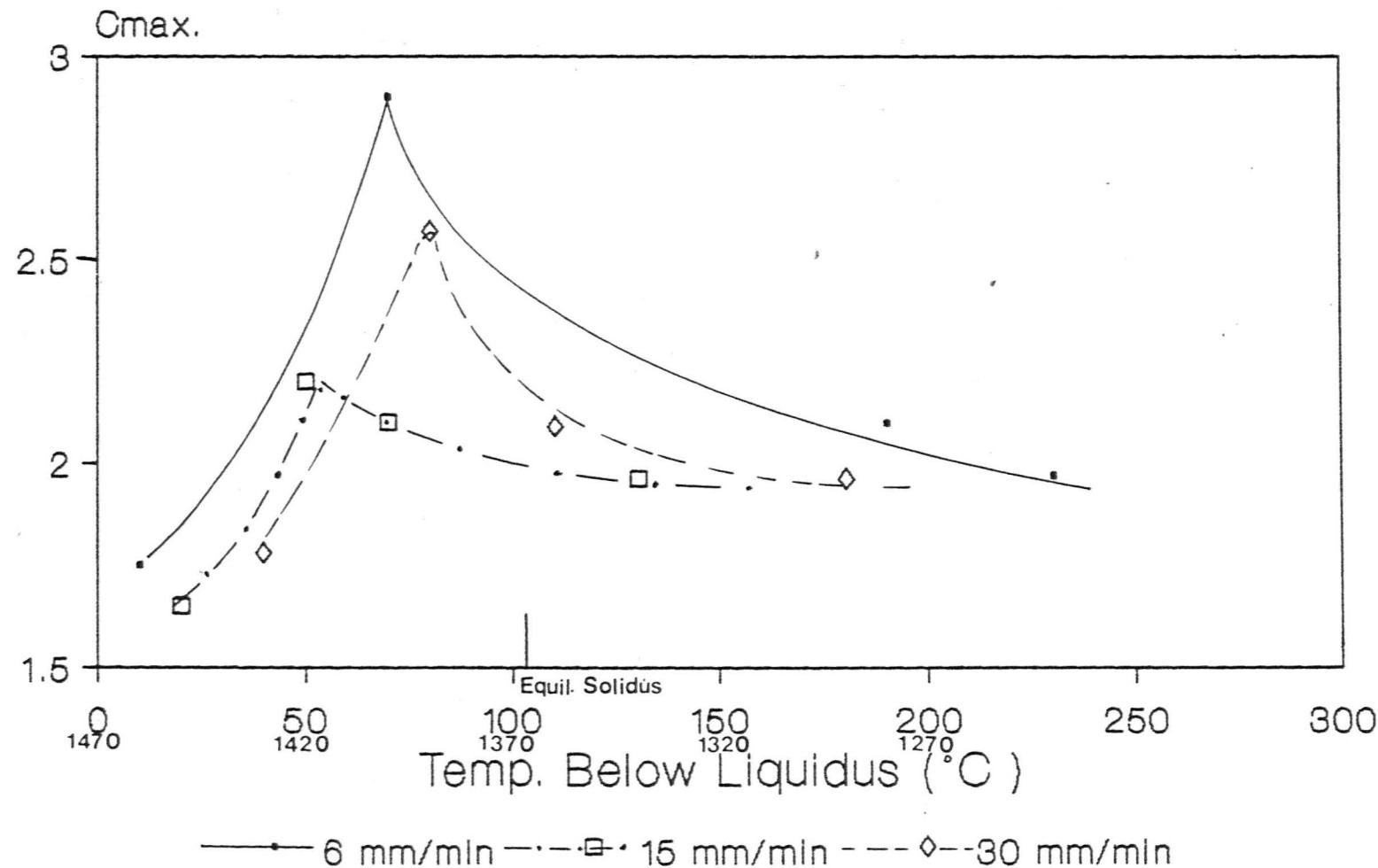
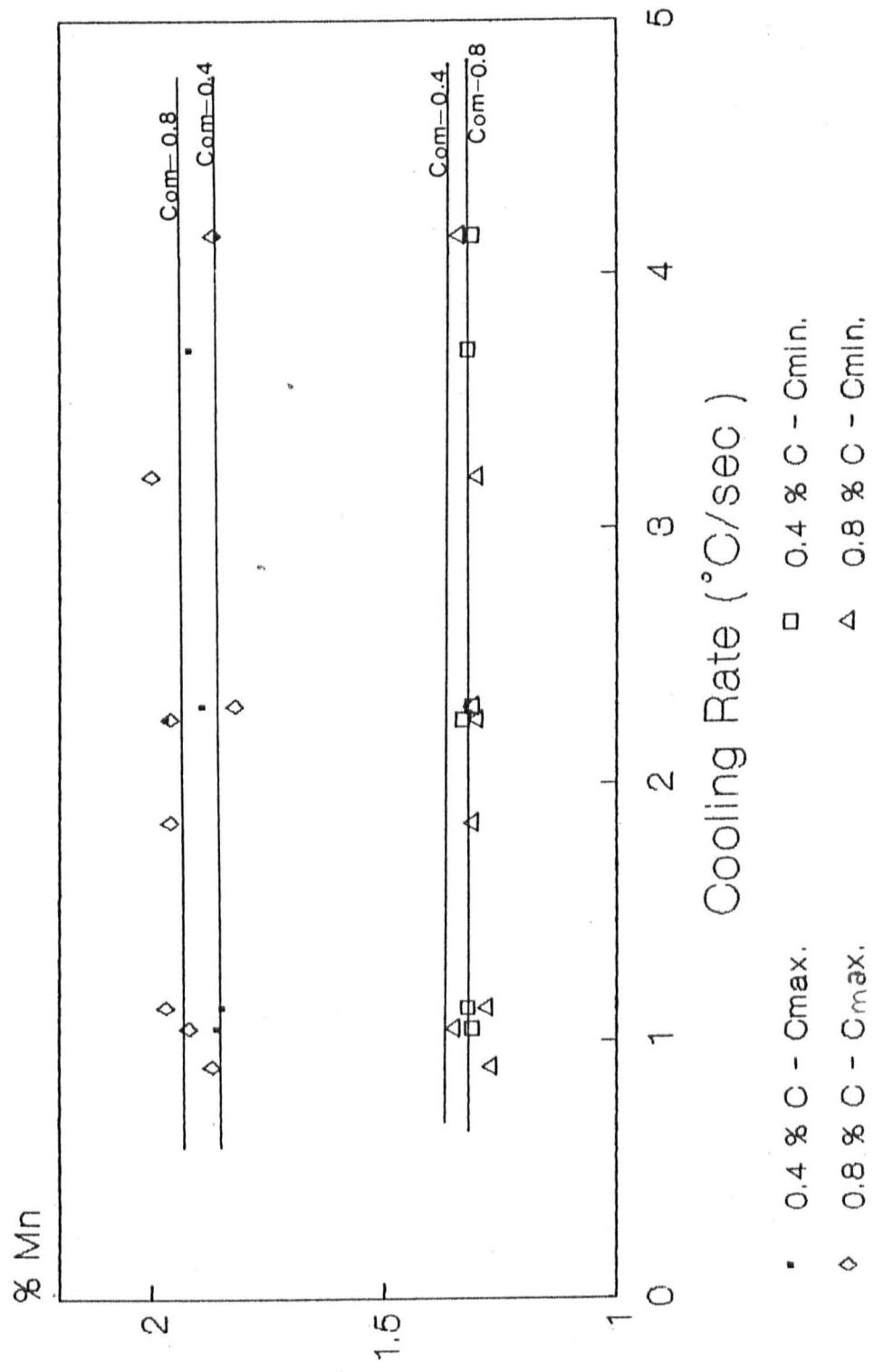


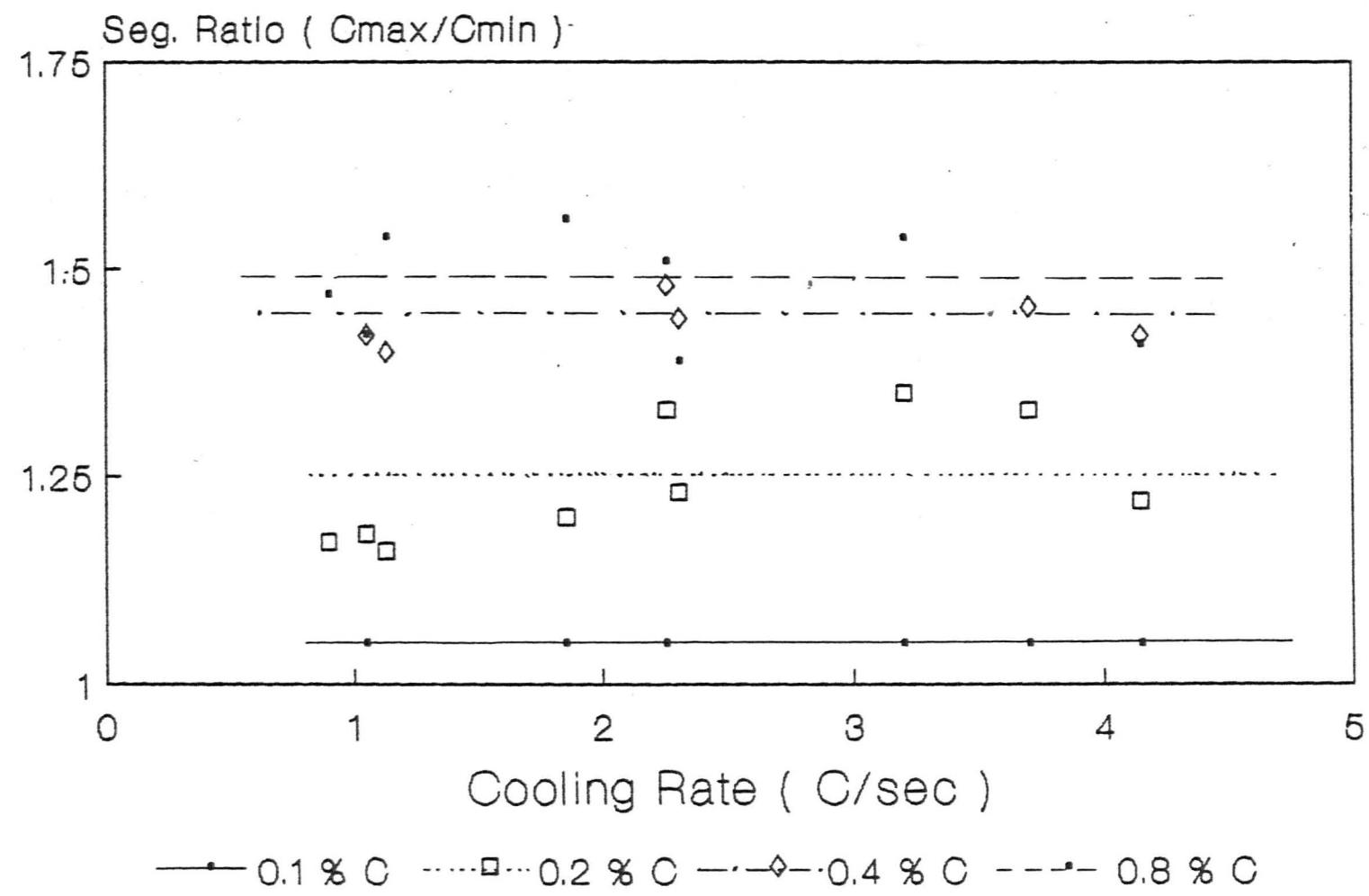
Figure 65

C_{max} and C_{min} as a function of cooling rate for 0.4 and 0.8 % C



1200°C

Figure 66
Segregation ratio between secondary arms as a function of
cooling rate and carbon content



1200 C

Figure 67

The secondary arm migration distance as a function of growth
rate

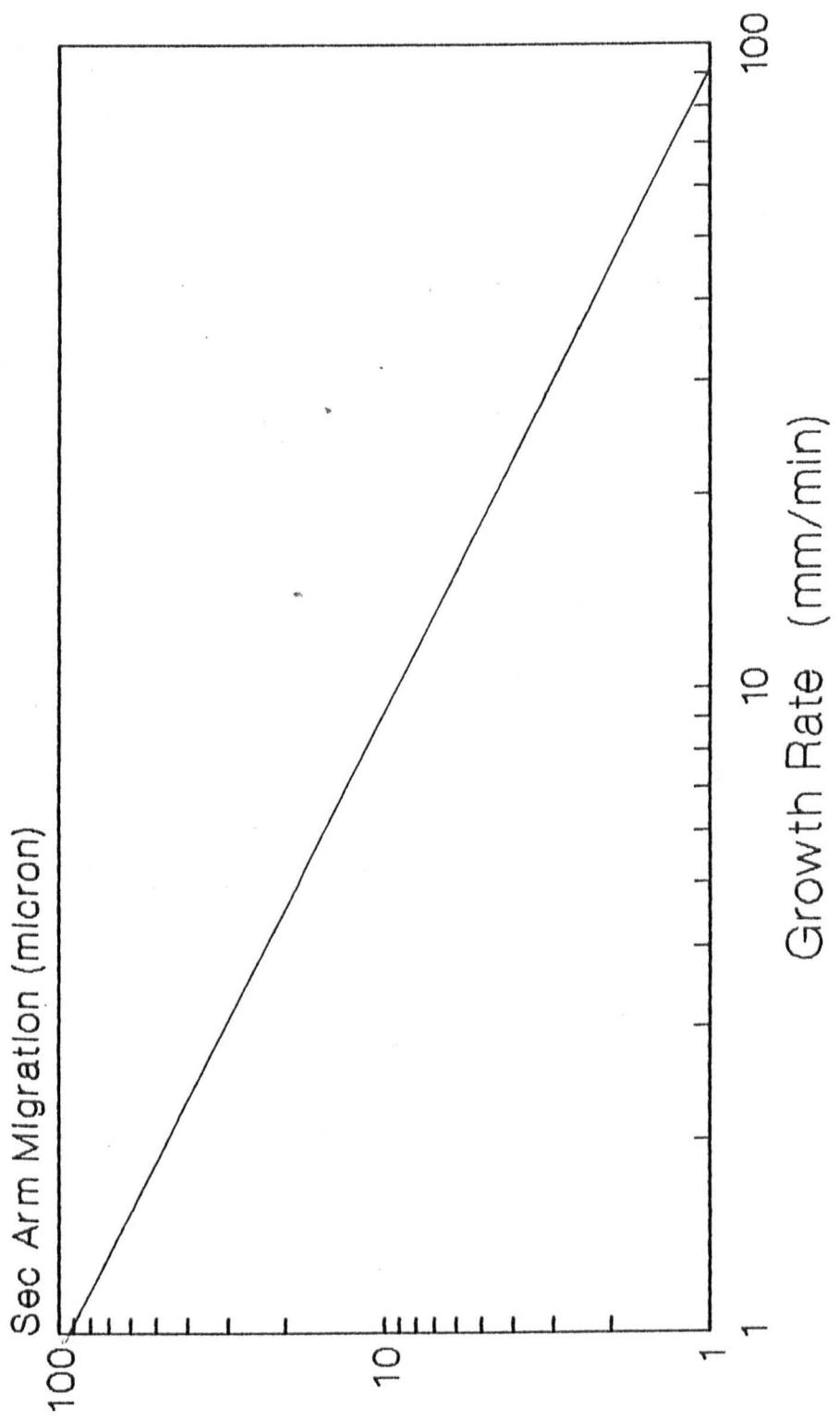


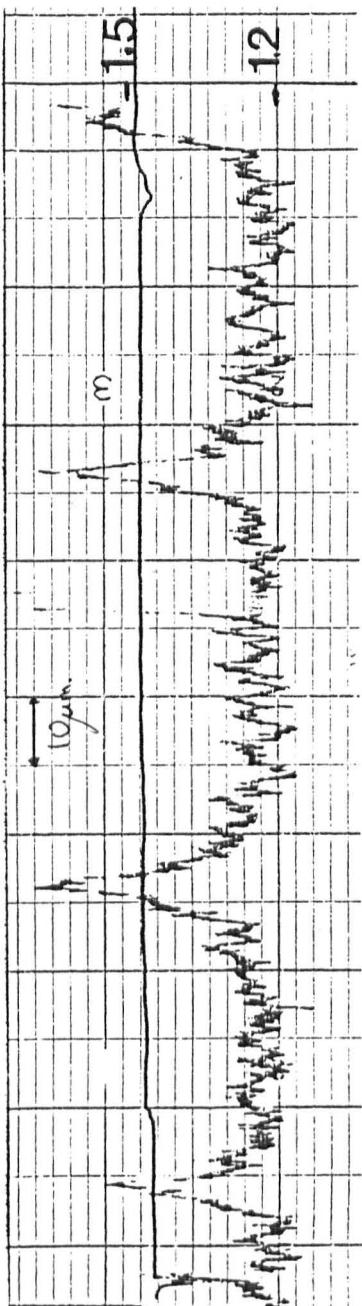
Figure 68

Electron micro probe concentration profiles through the
secondary arms (figure 54)

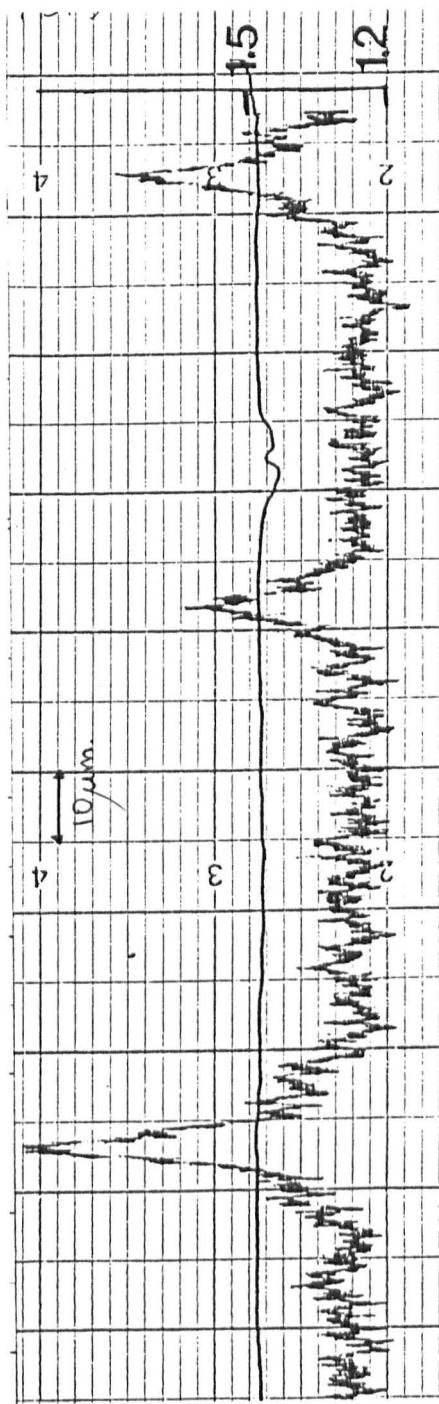
0.8 % C - 1.6 % Mn - Fe

Growth rate 1.5 mm/min

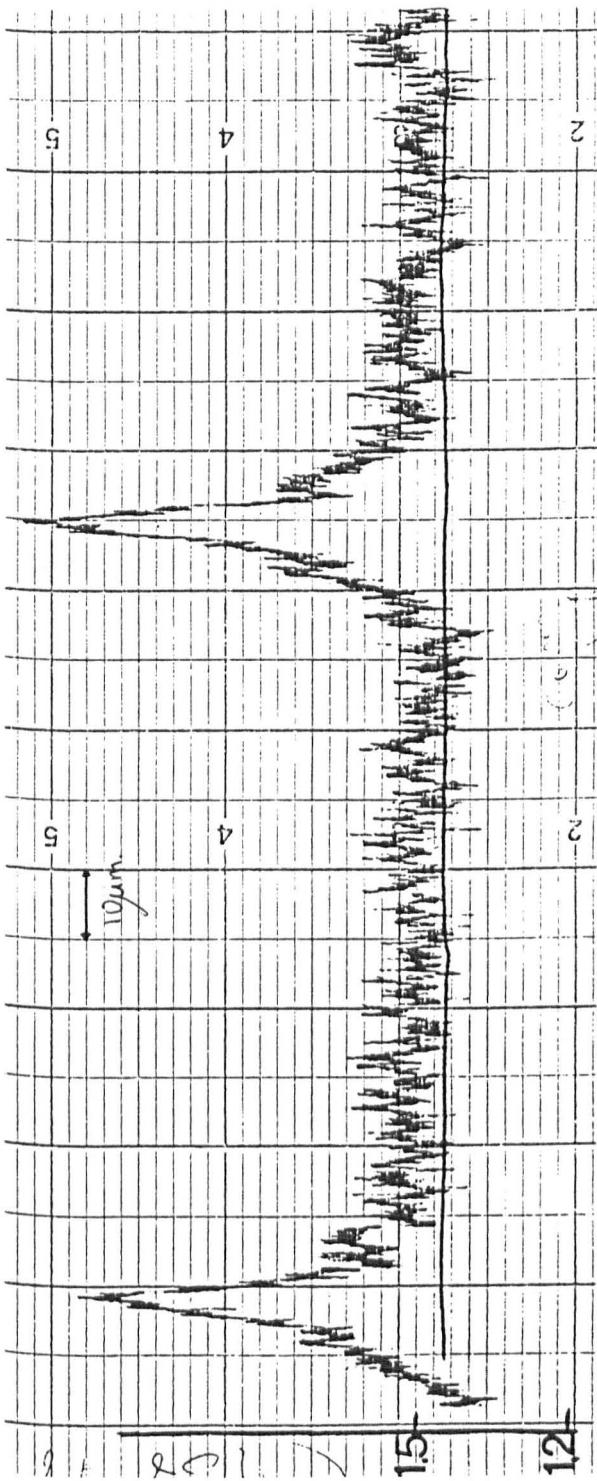
- a) 0.93 mm behind tips
- b) 2 mm behind tips
- c) 3.8 mm behind tips
- d) 6 mm behind tips
- e) 26 mm behind tips



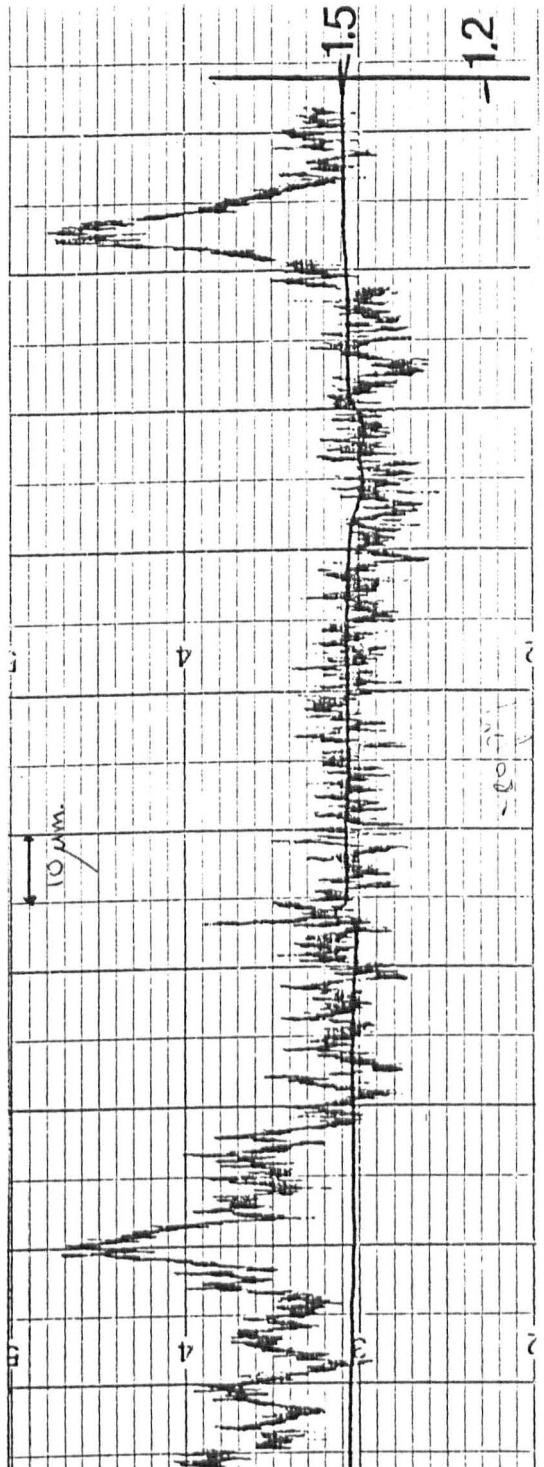
(A)



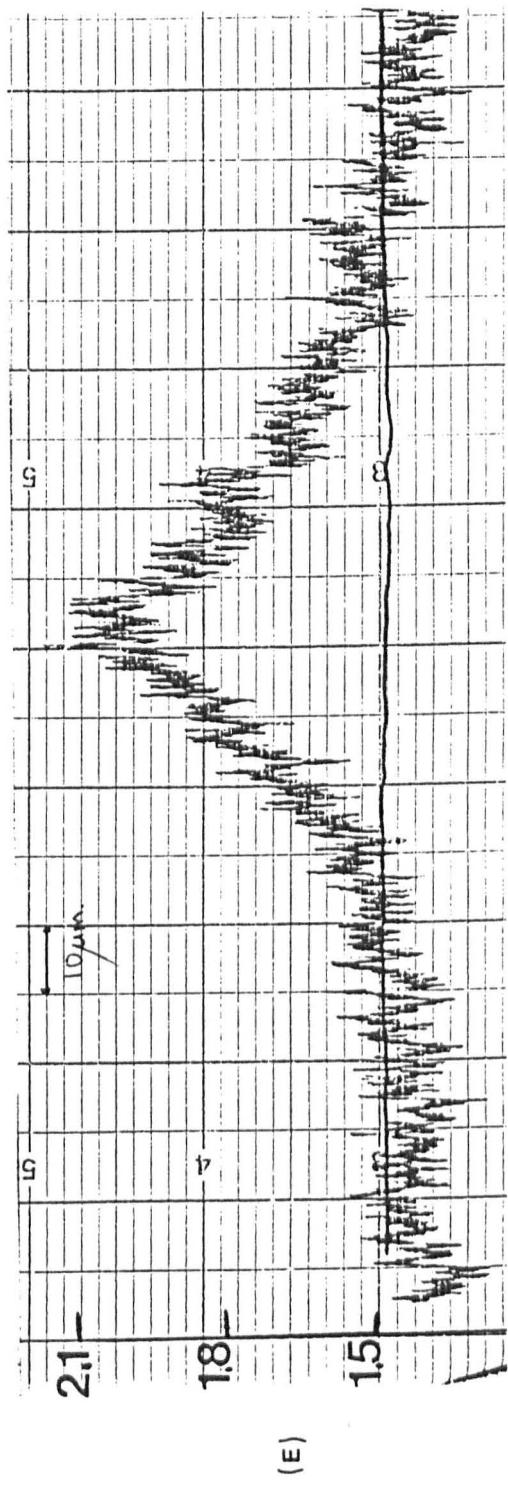
(B)



(c)



(d)



(E)

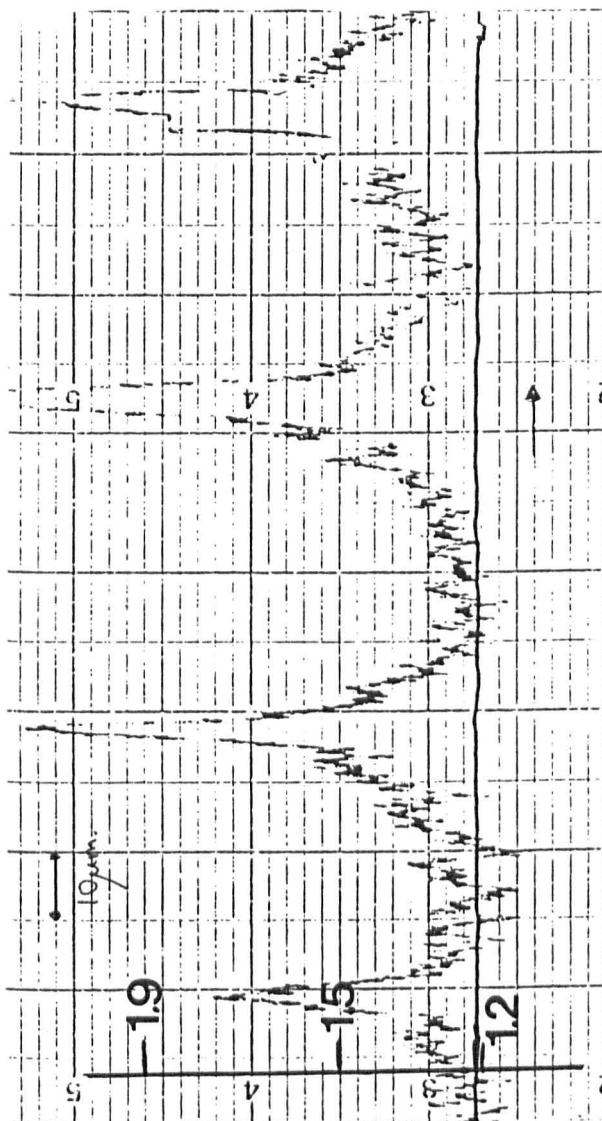
Figure 69

Electron micro probe concentration profiles through the secondary arms showing the TGZM effect (saw-tooth)

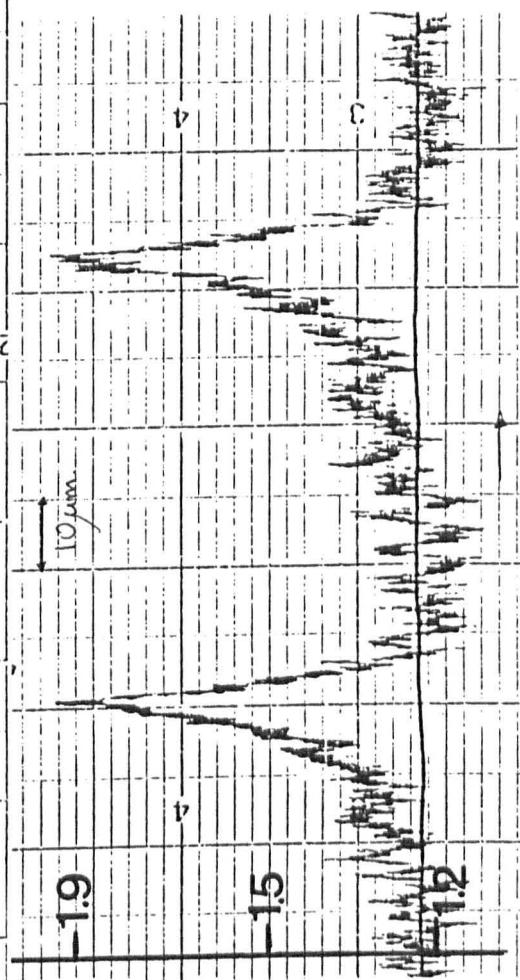
0.8 % C - 1.6 % Mn - Fe

Growth rate 6 mm/min

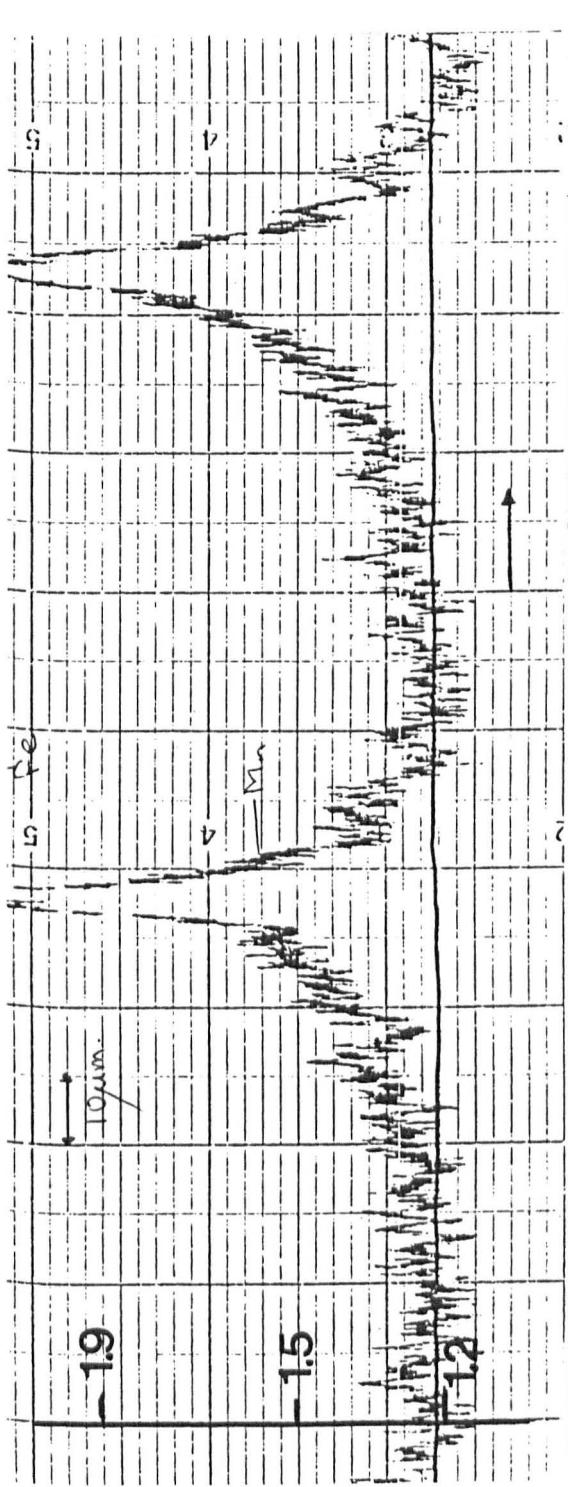
- a) 3.2 mm behind tips
- b) 5.6 mm behind tips
- c) 7.7 mm behind tips
- d) 13 mm behind tips
- e) after solidification complete



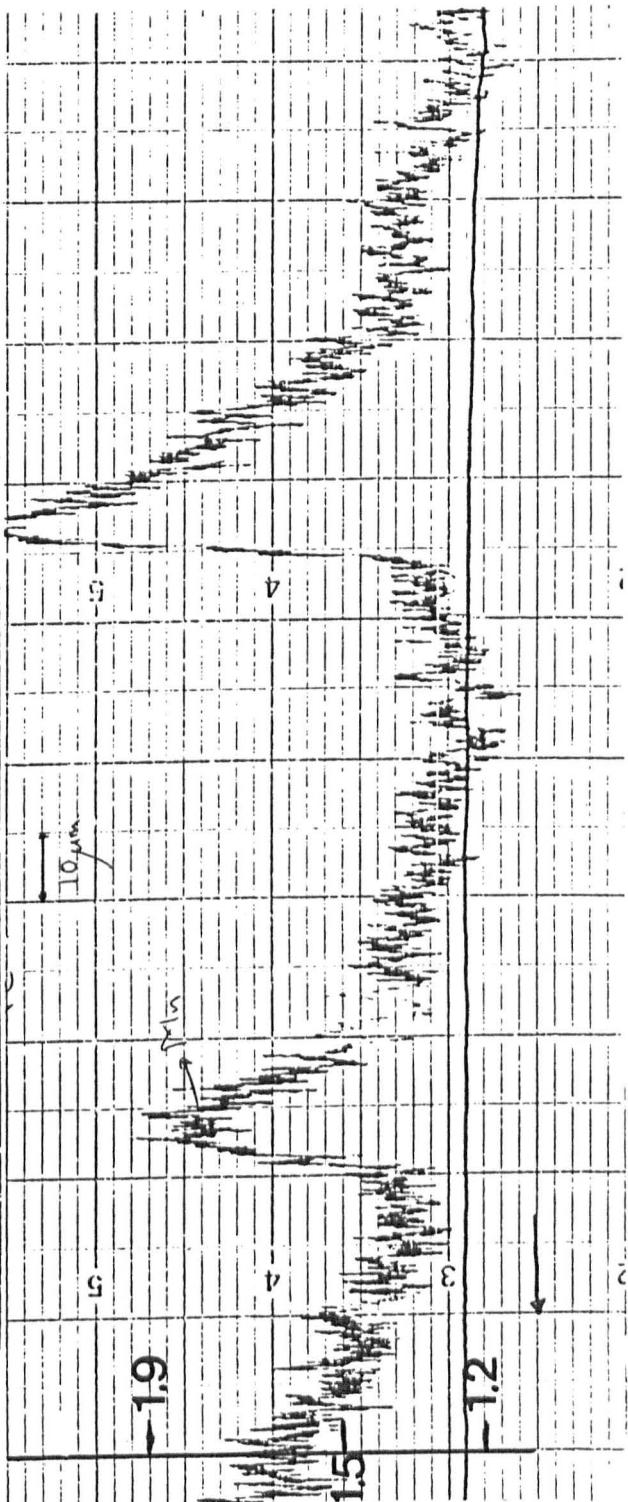
(A)



(B)



(c)



(d)

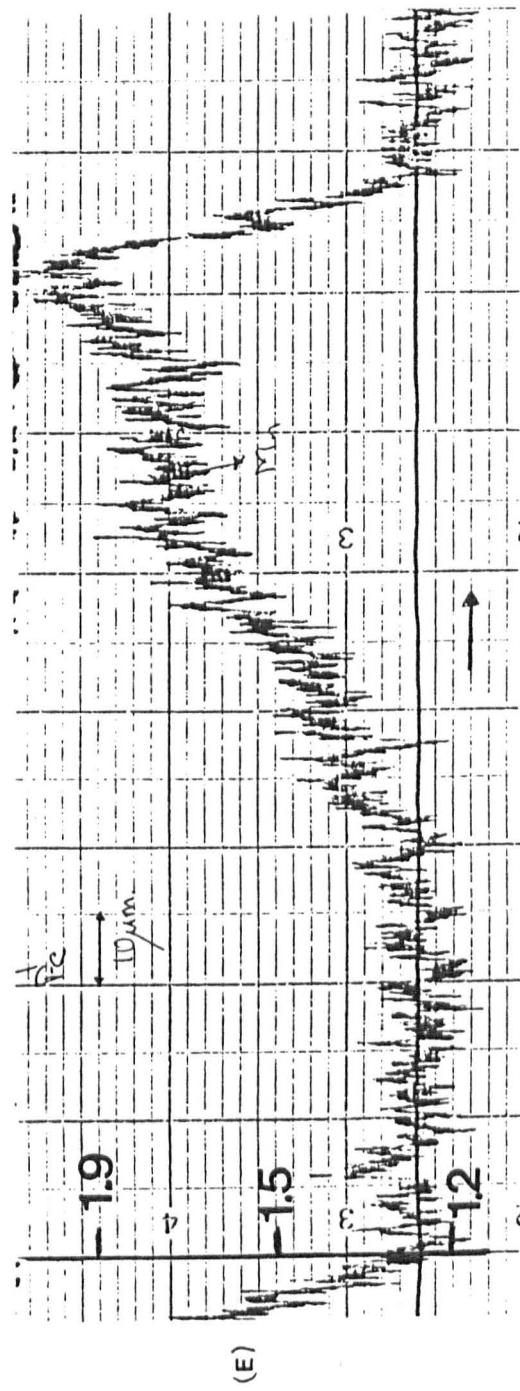


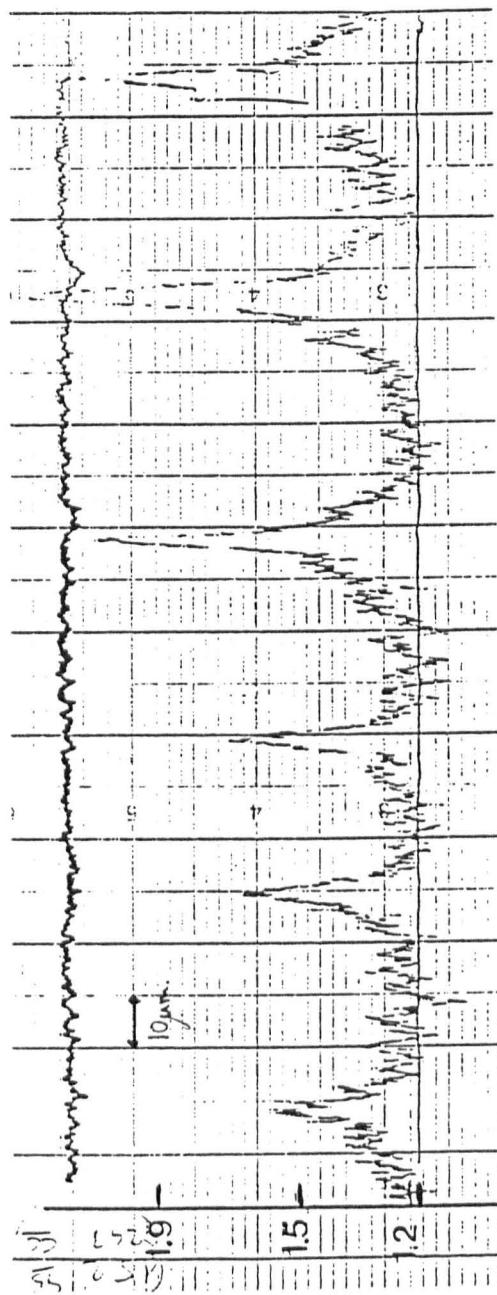
Figure 70

Electron micro probe concentration profiles through the
secondary arms showing the TGZM effect (saw-tooth)

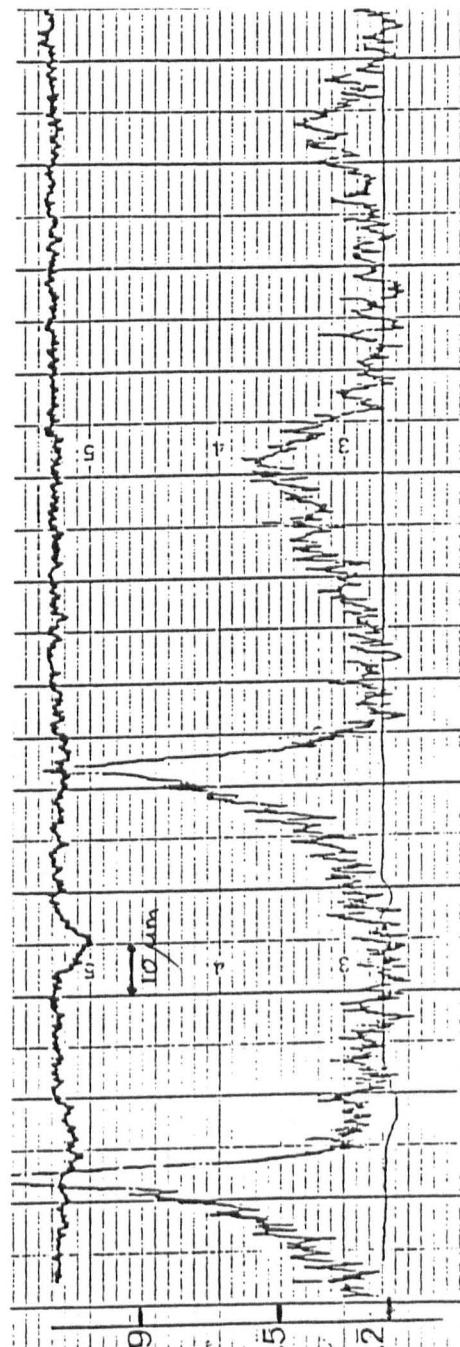
0.8 % C - 1.6 % Mn - Fe

Growth rate 15 mm/min

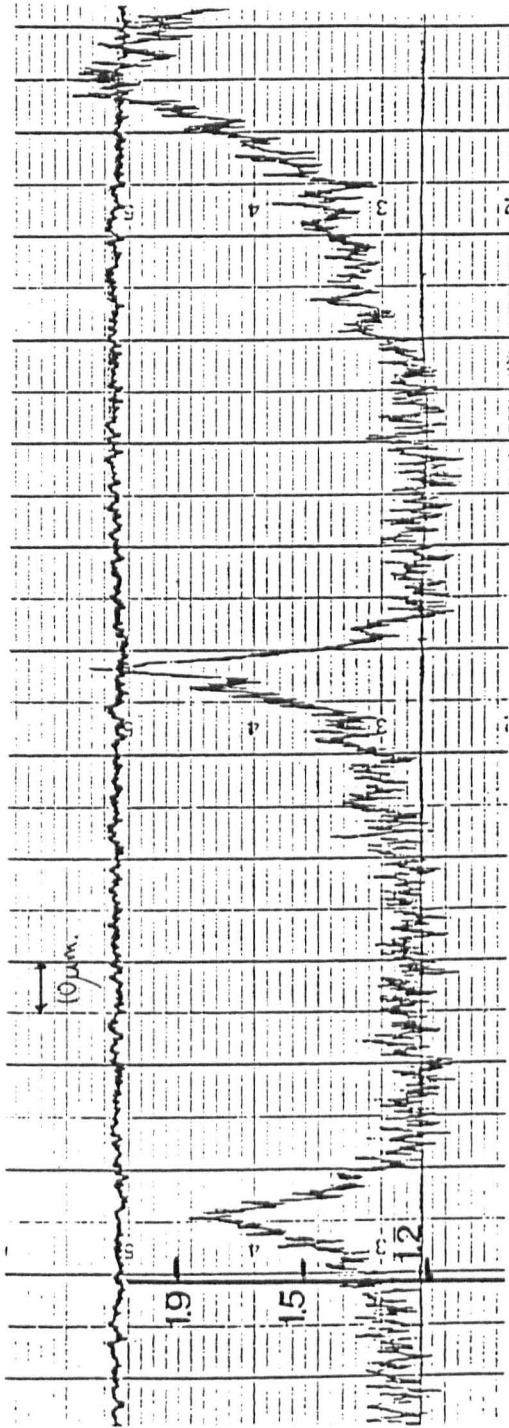
- a) 3.25 mm behind tips
- b) 15.5 mm behind tips
- c) 19 mm behind tips
- d) 26.5 mm beind tips



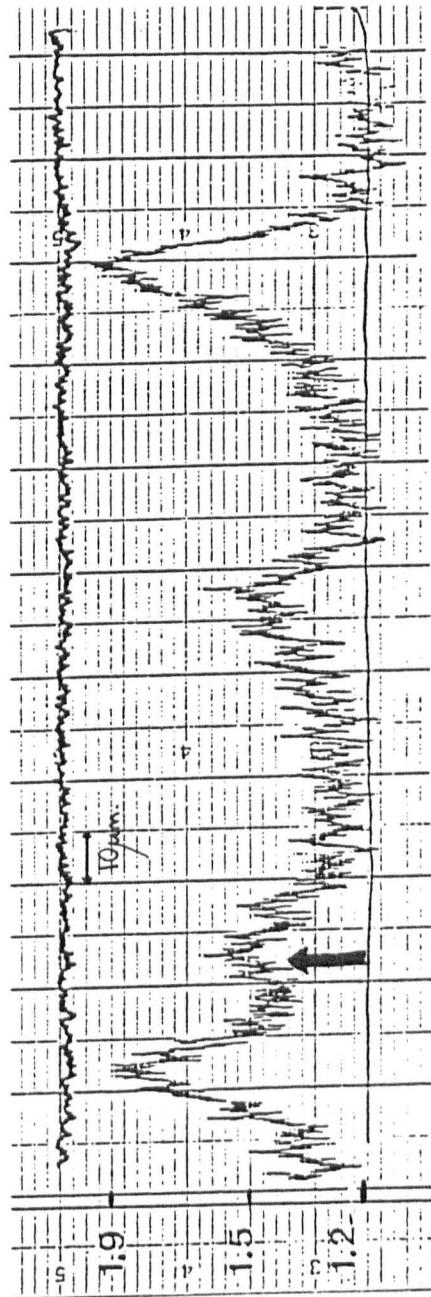
(A)



(B)



(c)



(d)

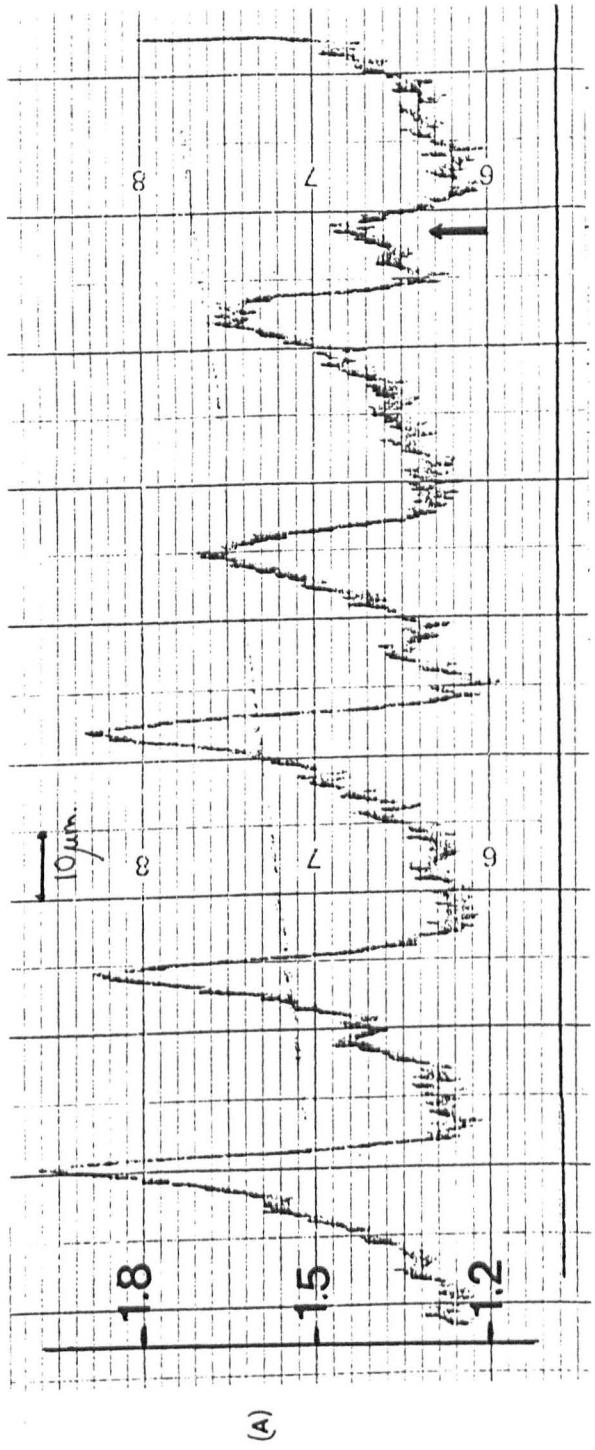
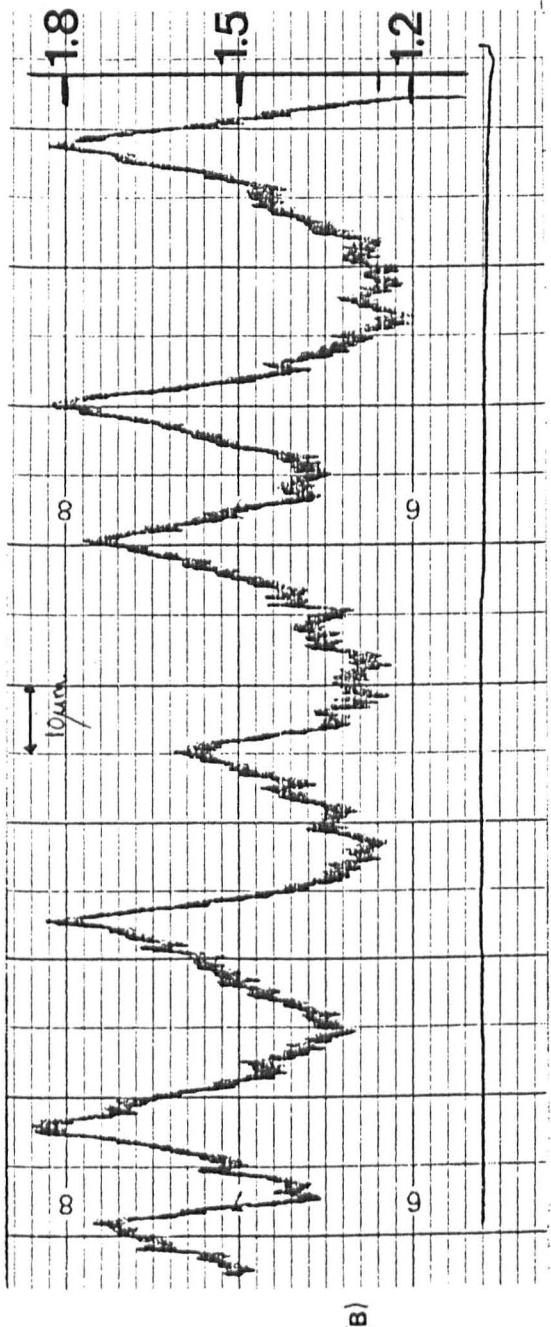
Figure 71

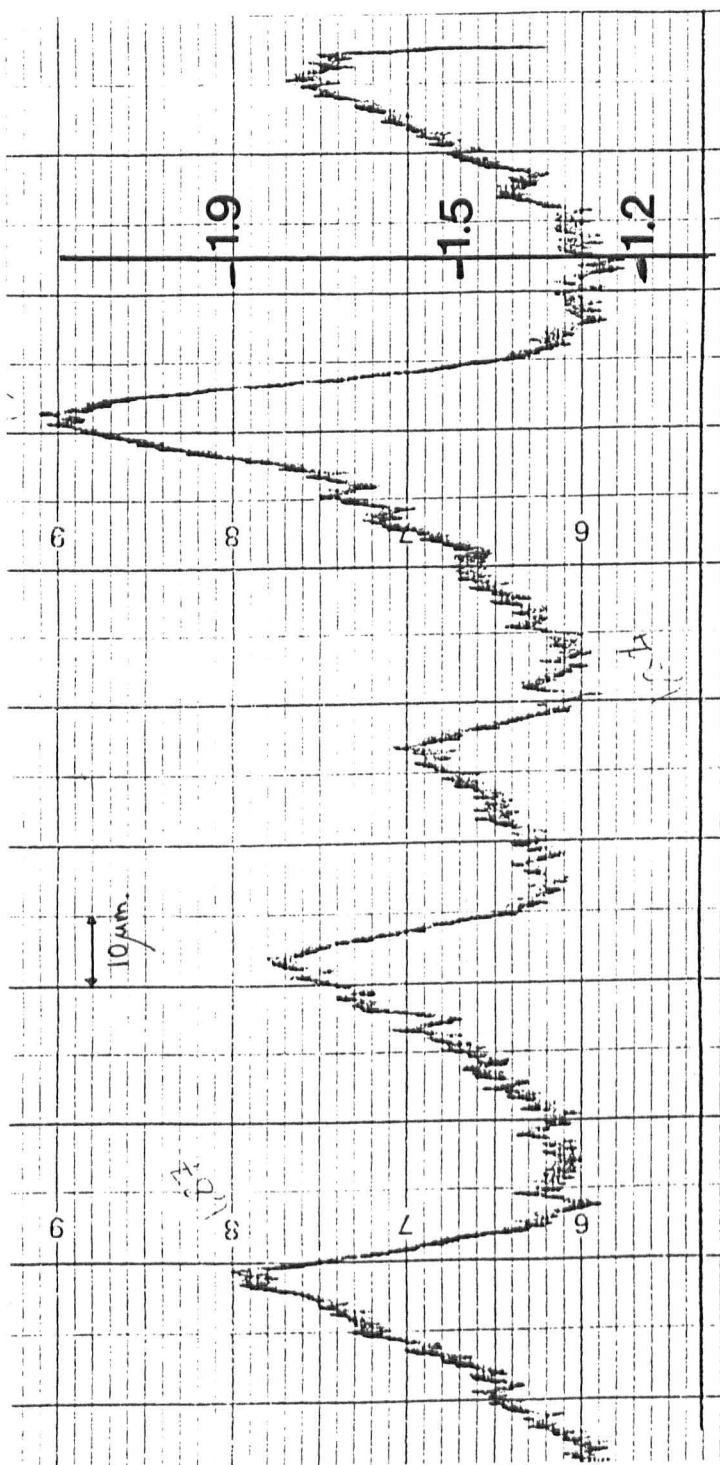
Electron micro probe concentration profiles through the secondary arms showing the TGZM effect (saw-tooth)

0.8 % C - 1.6 % Mn - Fe

Growth rate 30 mm/min

- a) 3 mm behind tips**
- b) 7 mm behind tips**
- c) 23 mm behind tips**





c

Figure 72

The change of the minimum concentration of manganese as a function of temperature below liquidus for 0.1 % C and 0.2 % C at the 1.5 and 6 mm/min growth rate

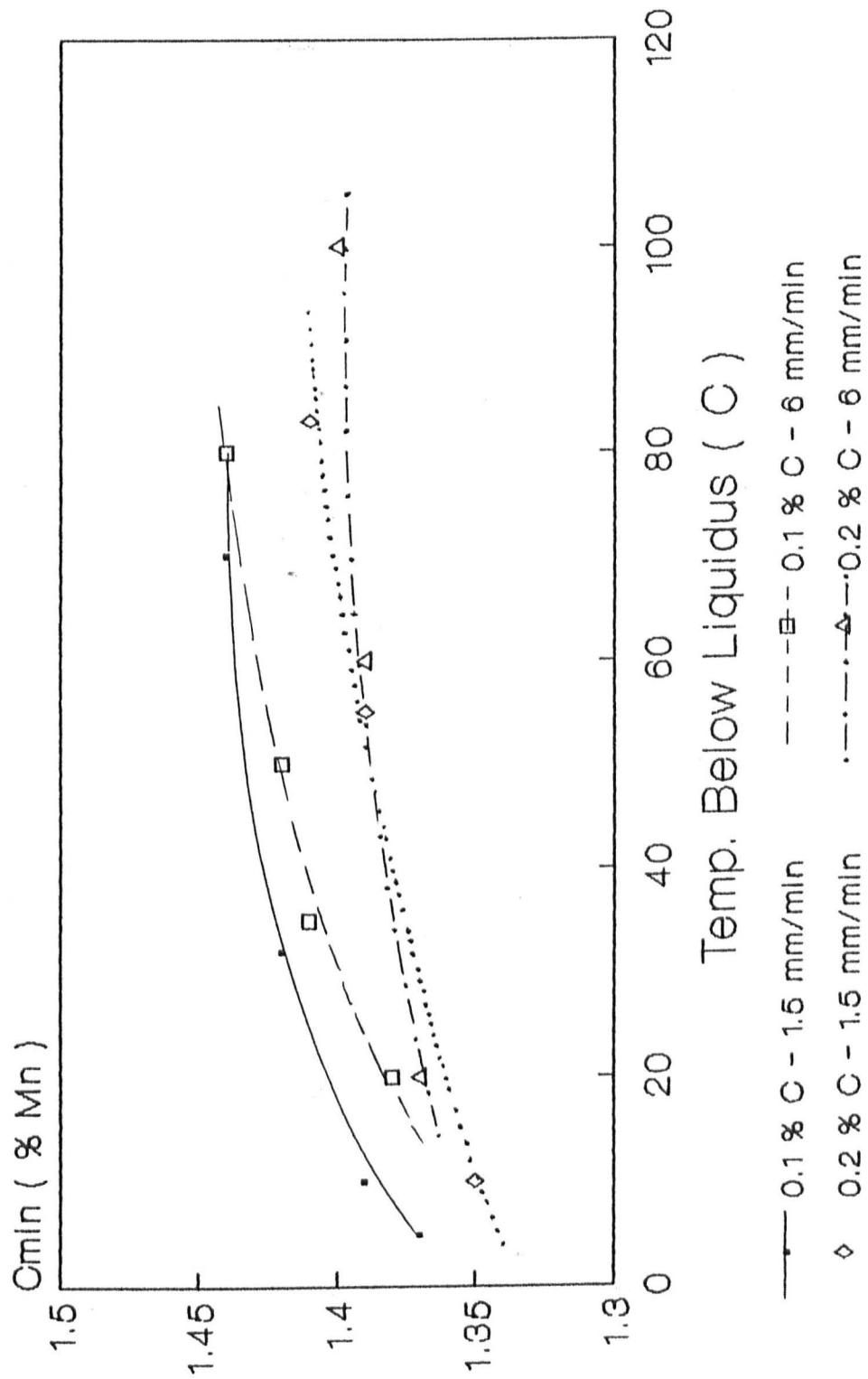
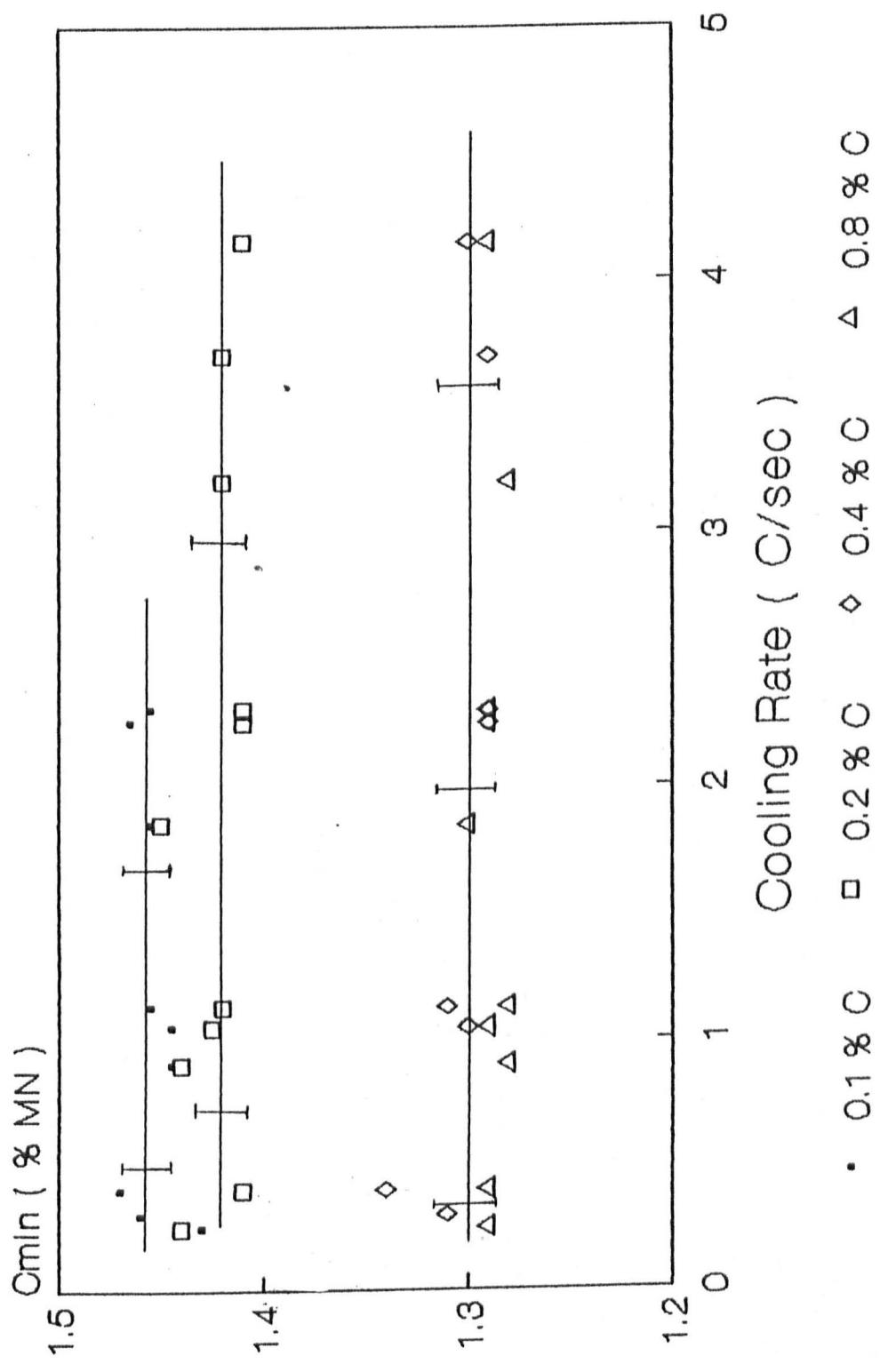


Figure 73

The minimum concentration of manganese as a function of
cooling rate for different carbon contents



Variation of the maximum concentration of manganese and the computer results as a function of cooling rate for

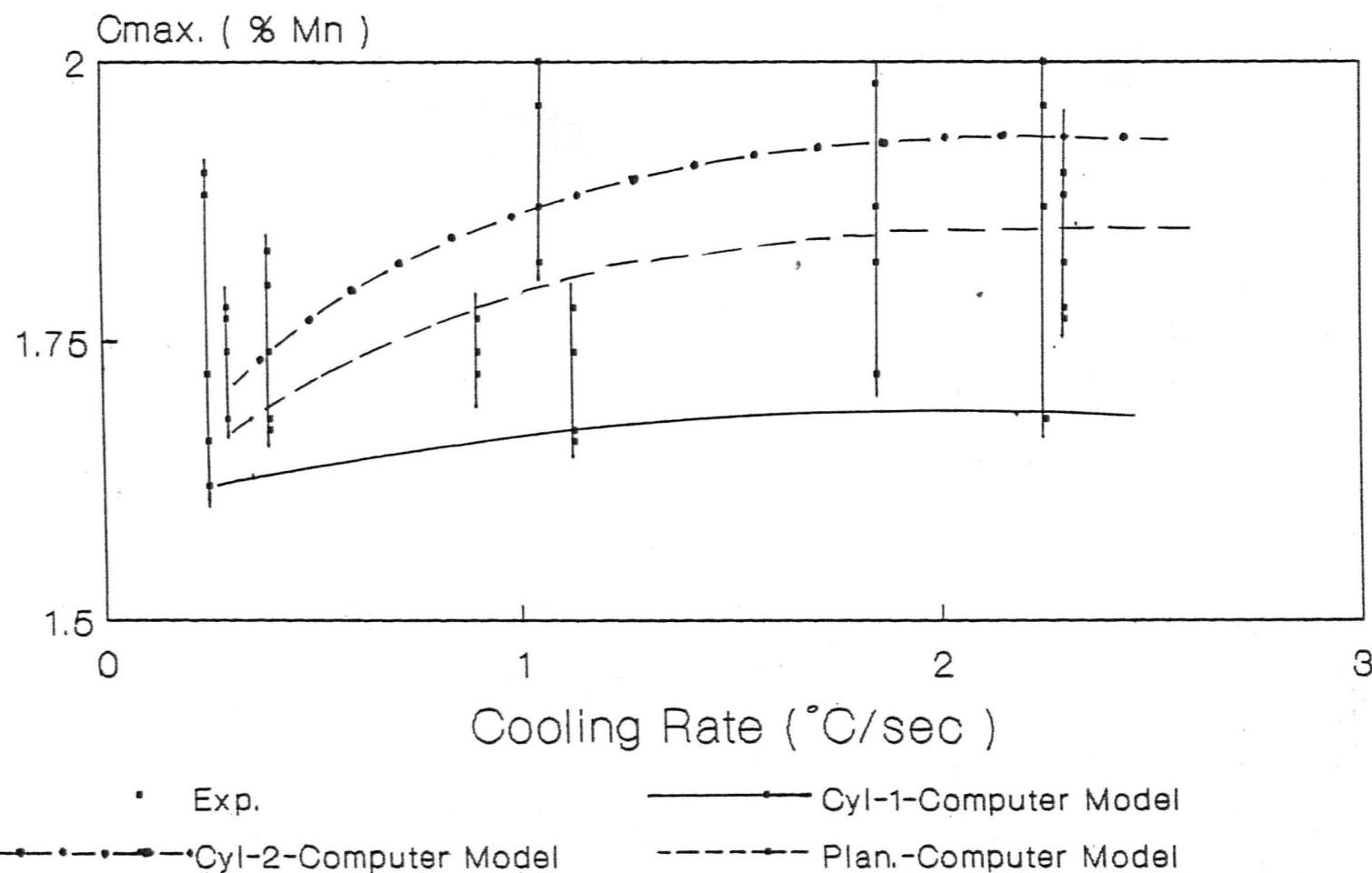
Figure 74 - 0.1 % C

Figure 75 - 0.2 % C

Figure 76 - 0.4 % C

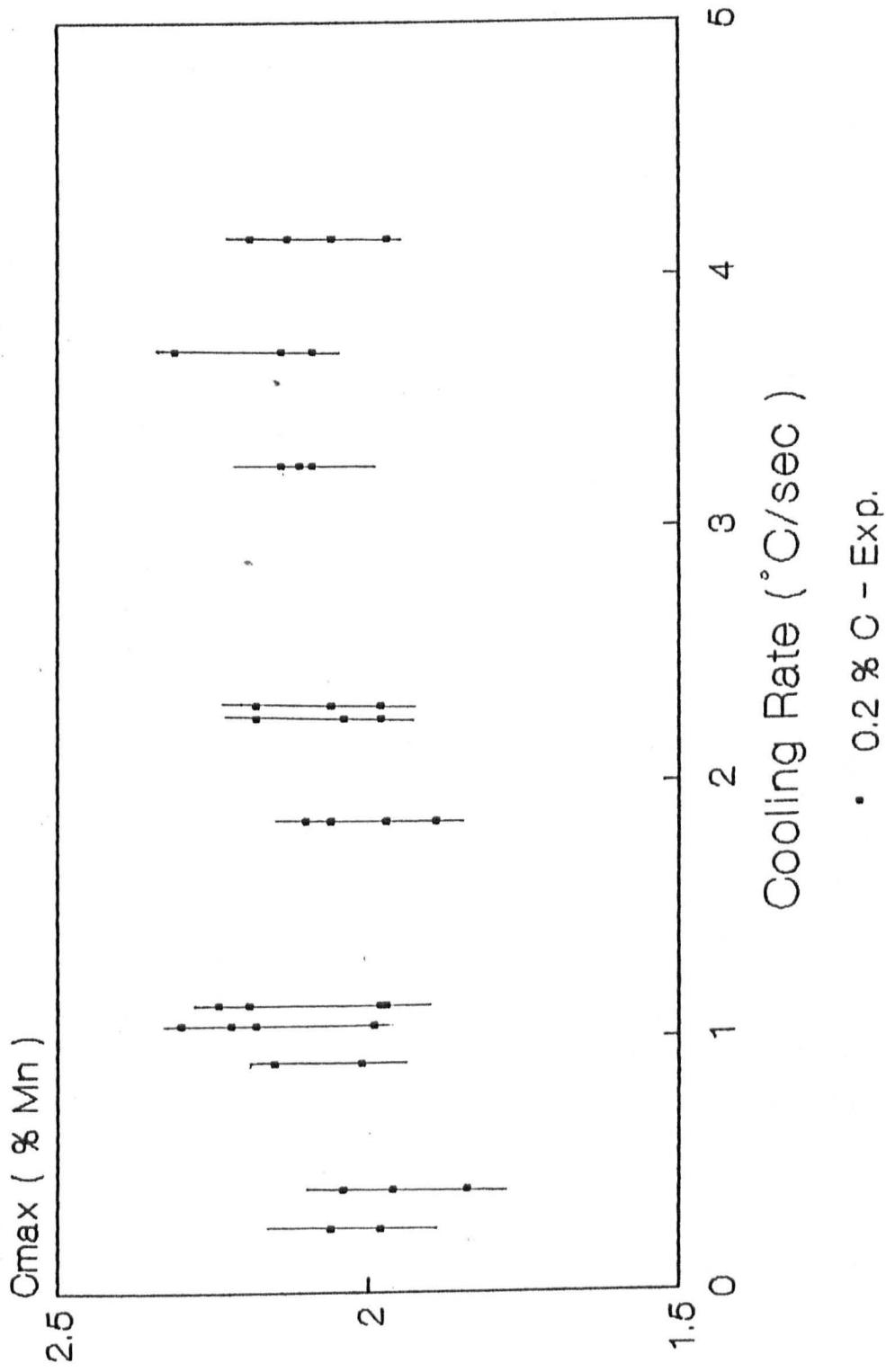
Figure 77 - 0.8 % C

Figure 78 - 0.8 % C , 0.4 % C, 0.2 % C and 0.1 % C



1485°C - 0.1% C

Figure 74



1200°C

Figure 75

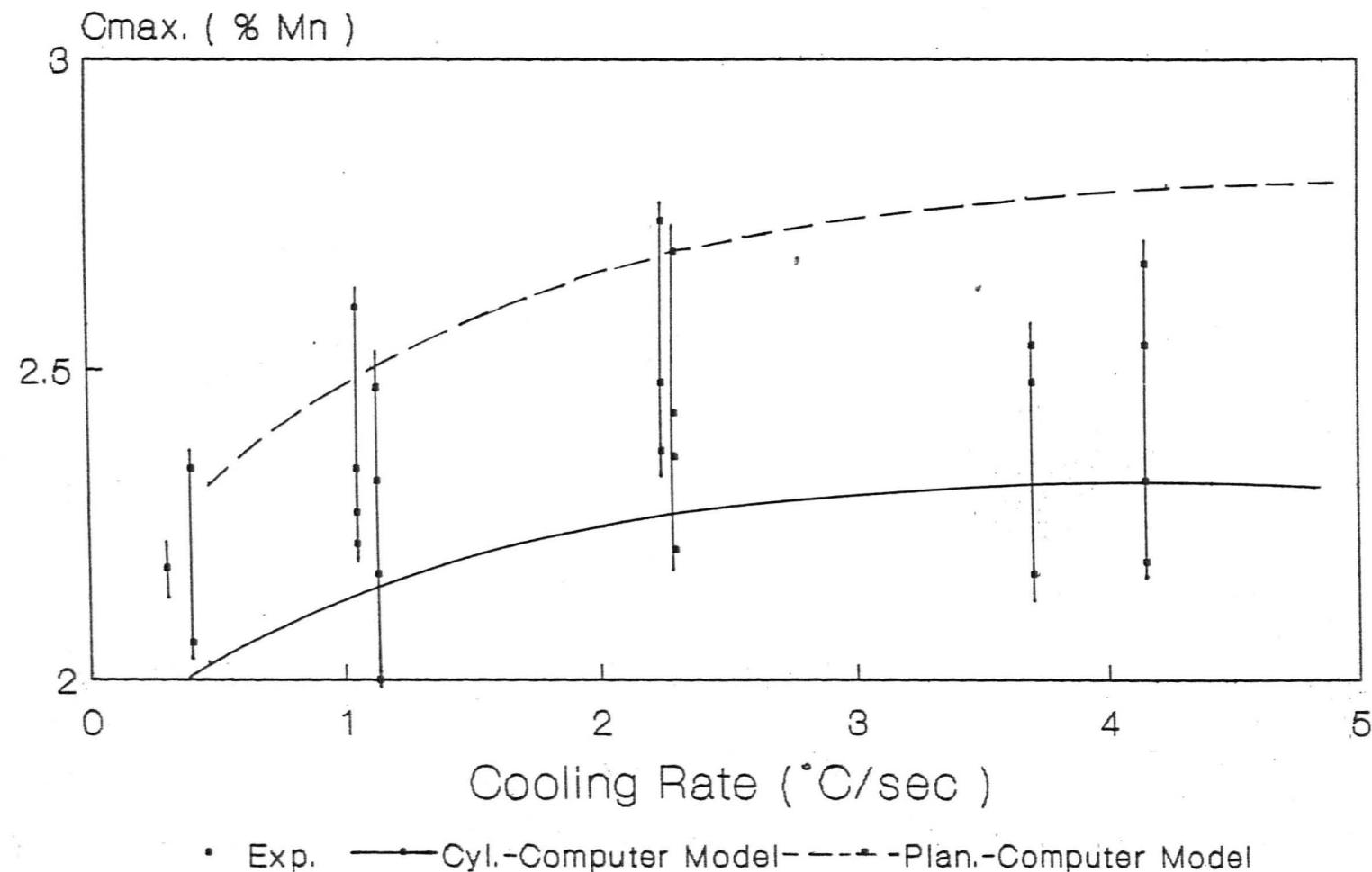


Figure 76

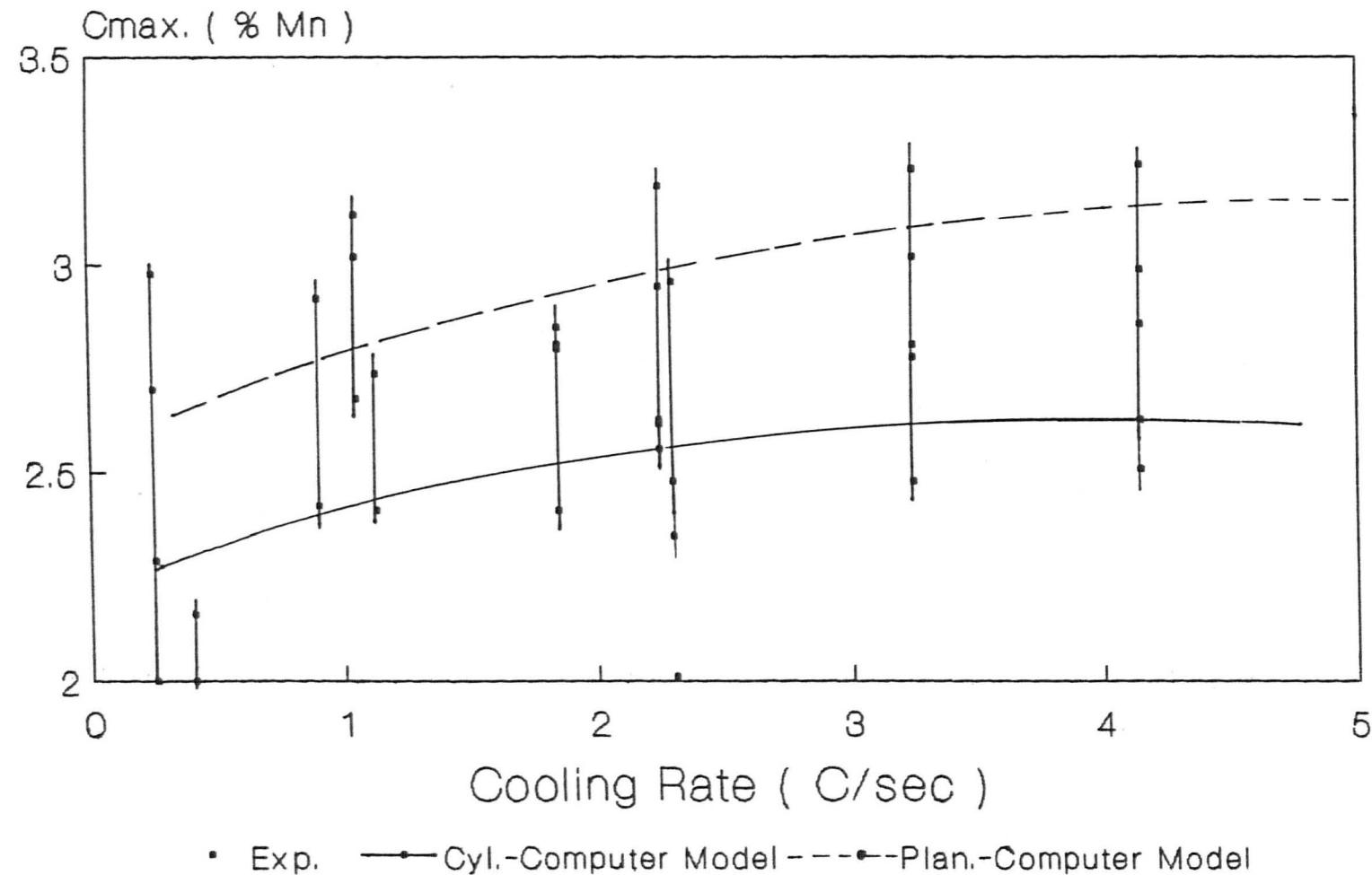


Figure 77

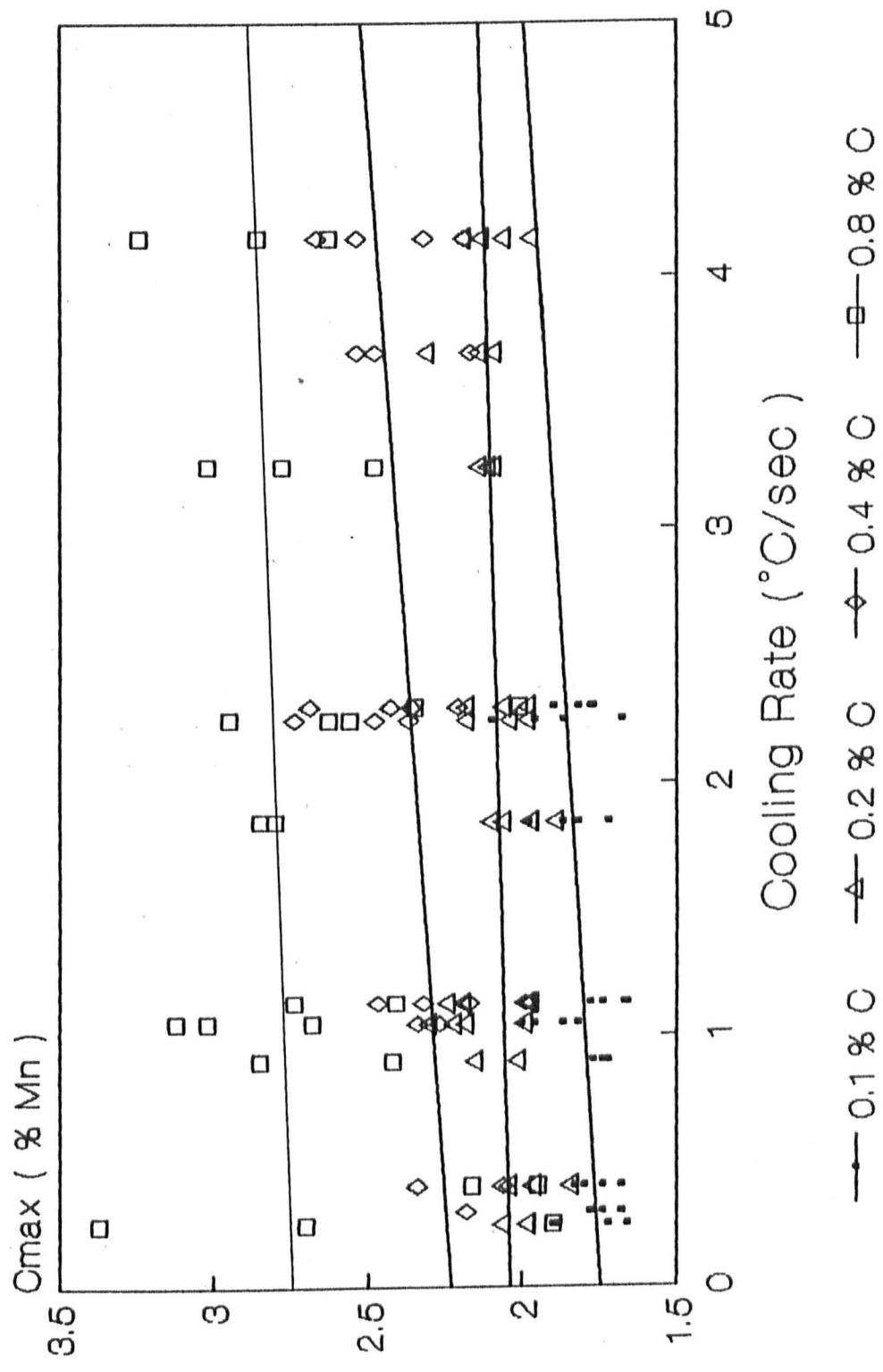
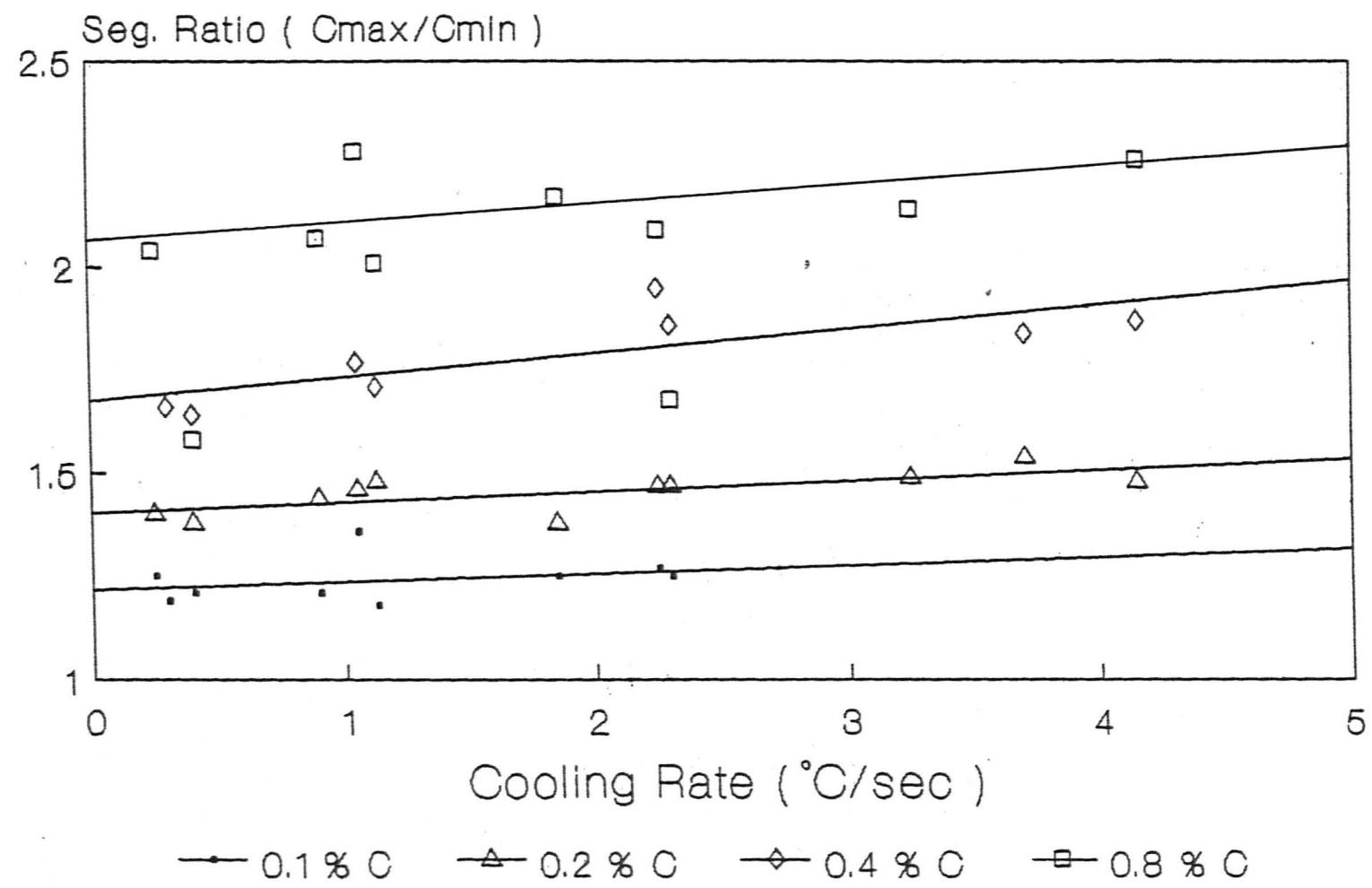


Figure 78

Figure 79

The segregation ratio of manganese as a function of cooling rate and carbon content



1200°C

Colour concentration maps of primary arms at the different concentration range indicating the concave solidification points

Figure 80

0.8 % C - 1.6 Mn - Fe

Growth rate 1.5 mm/min

a) printed at low concentration range

b) printed at high concentration range

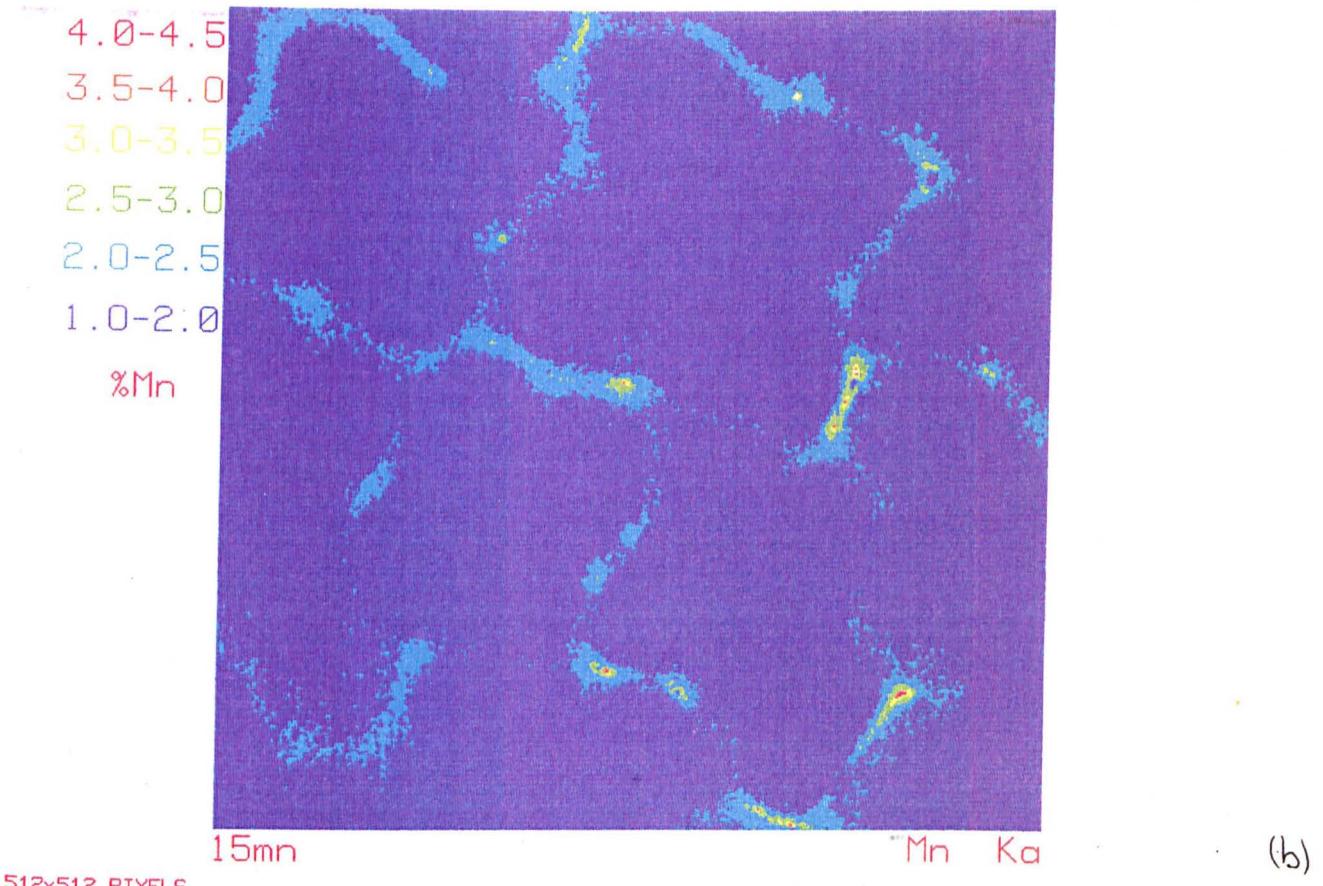
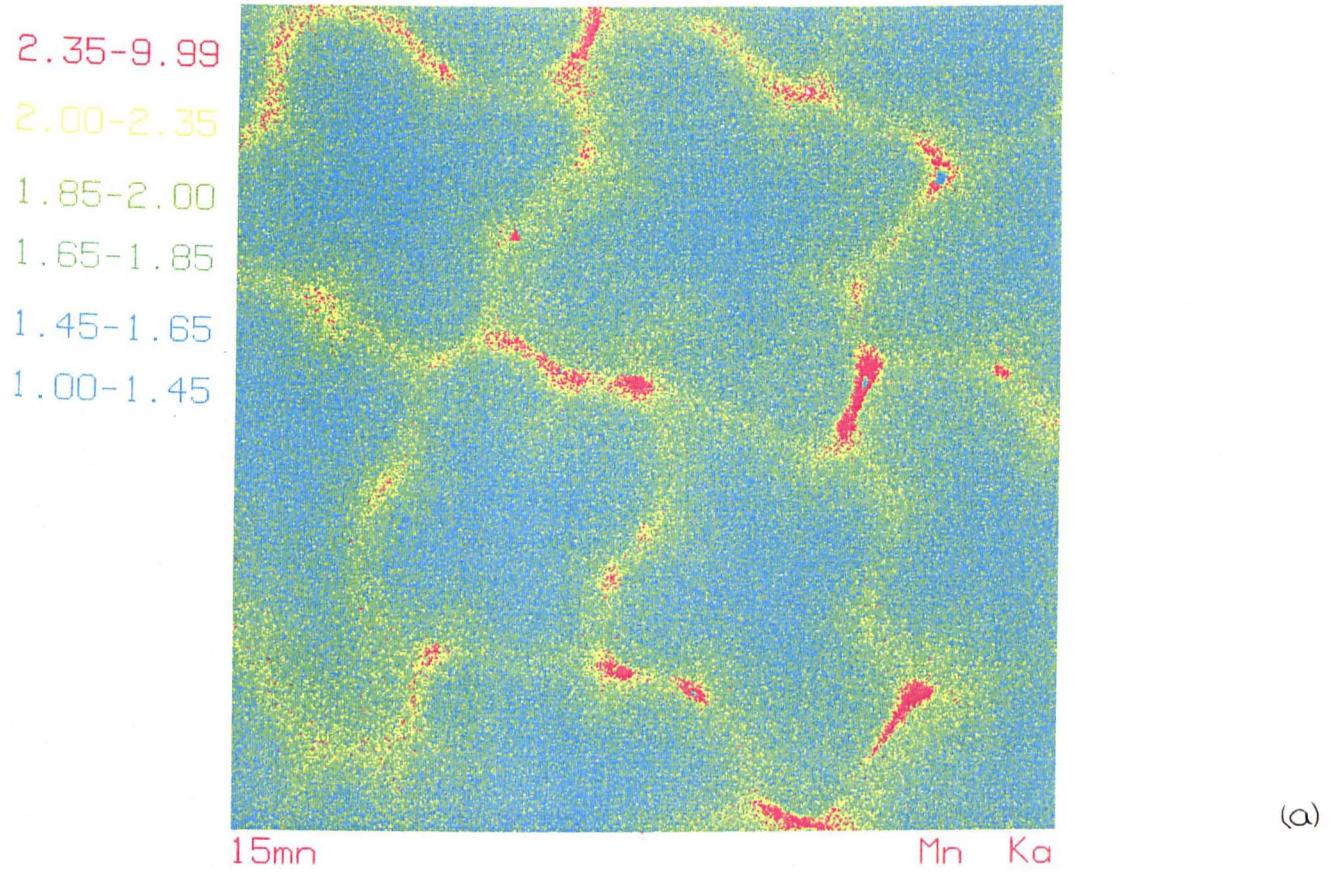
Figure 81

0.1 % C - 1.6 Mn - Fe

Growth rate 1.5 mm/min

a) printed at low concentration range

b) printed at high concentration range



512x512 PIXELS
001024x001024 μ

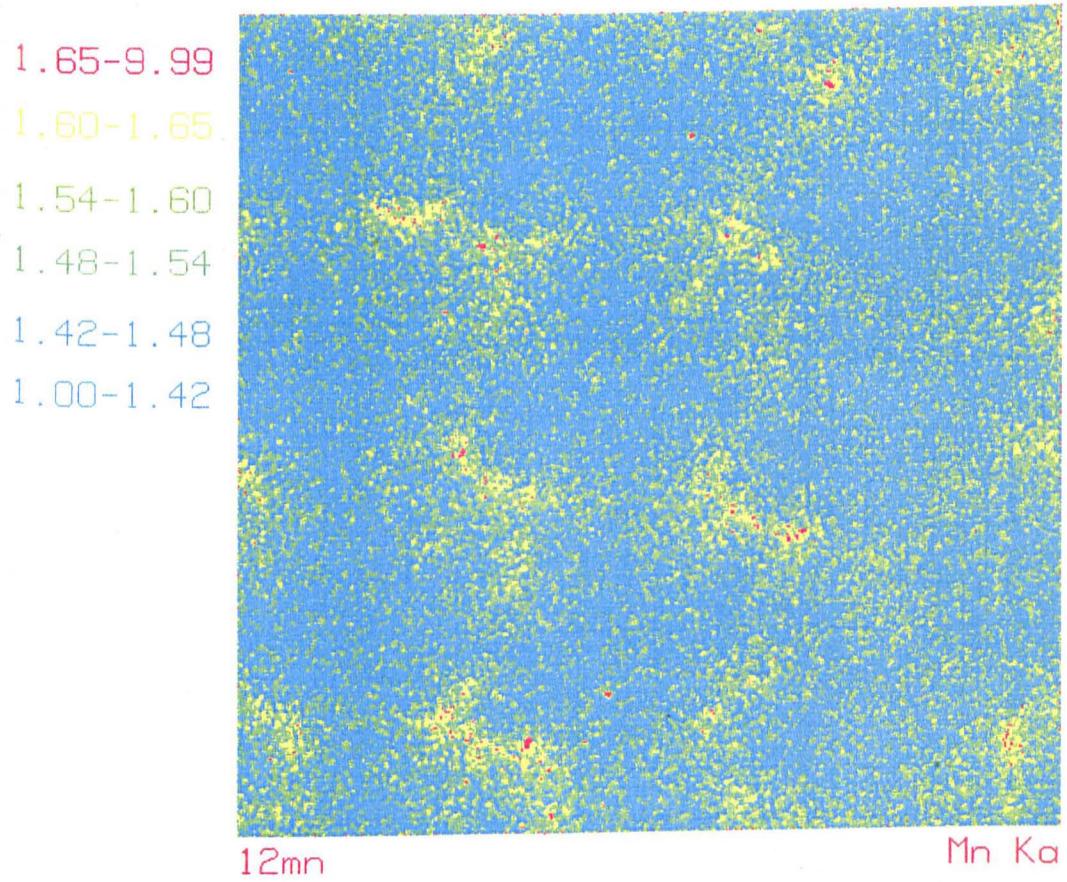
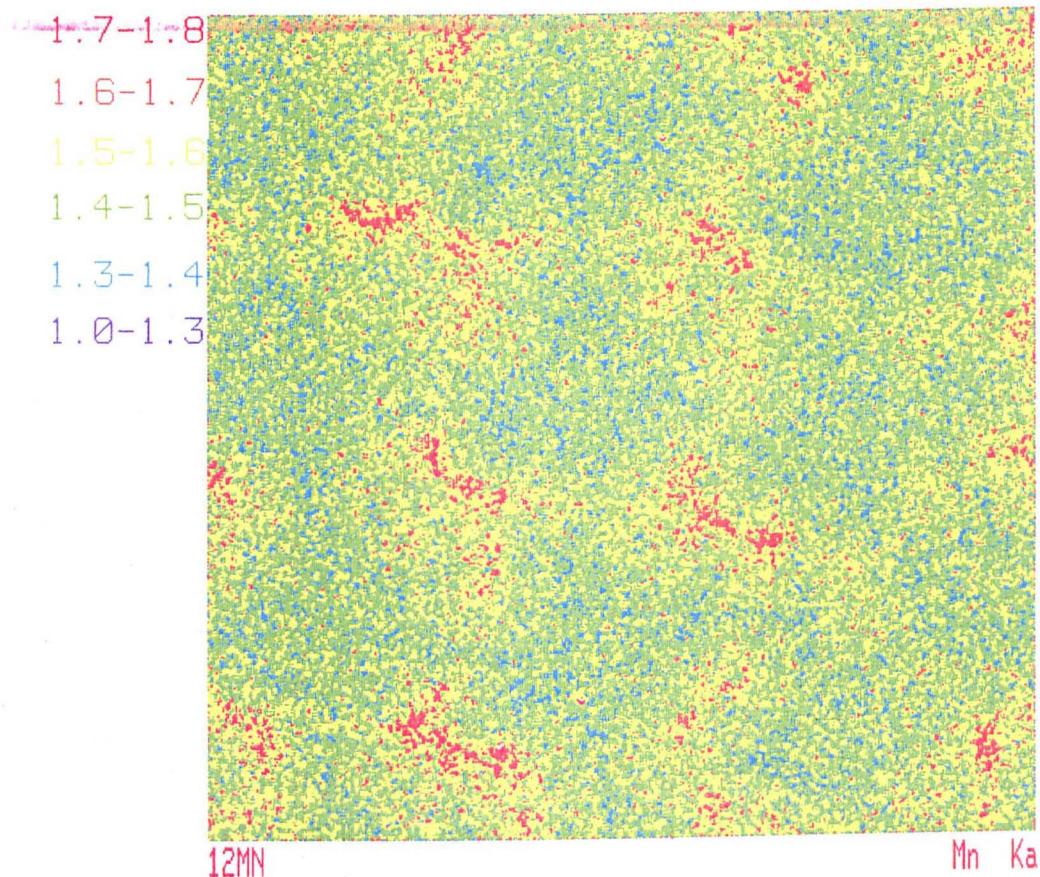
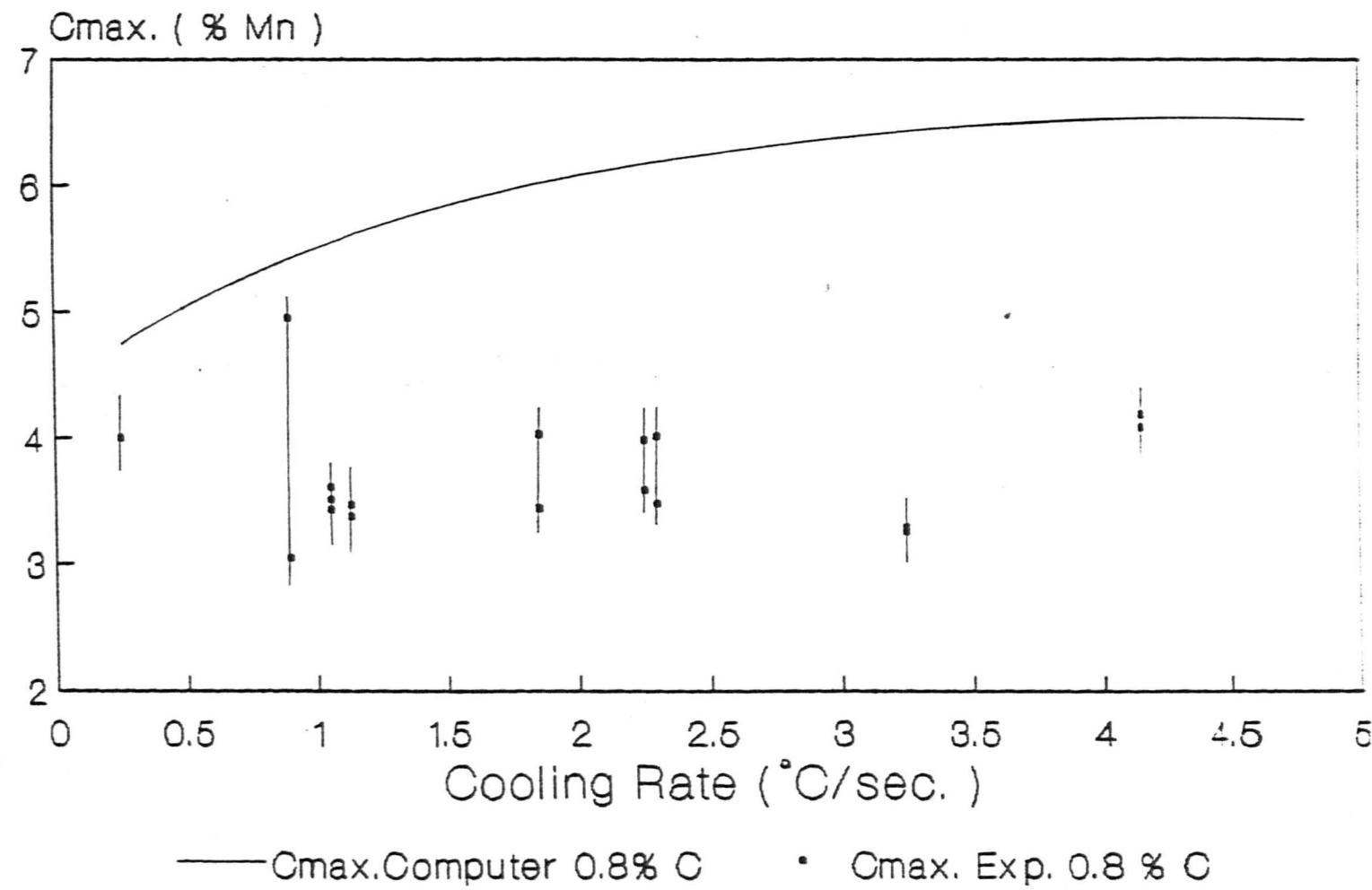


Figure 82

Comparison of predicted maximum concentration of manganese by concave computer model to the experimental results as a function of cooling rate

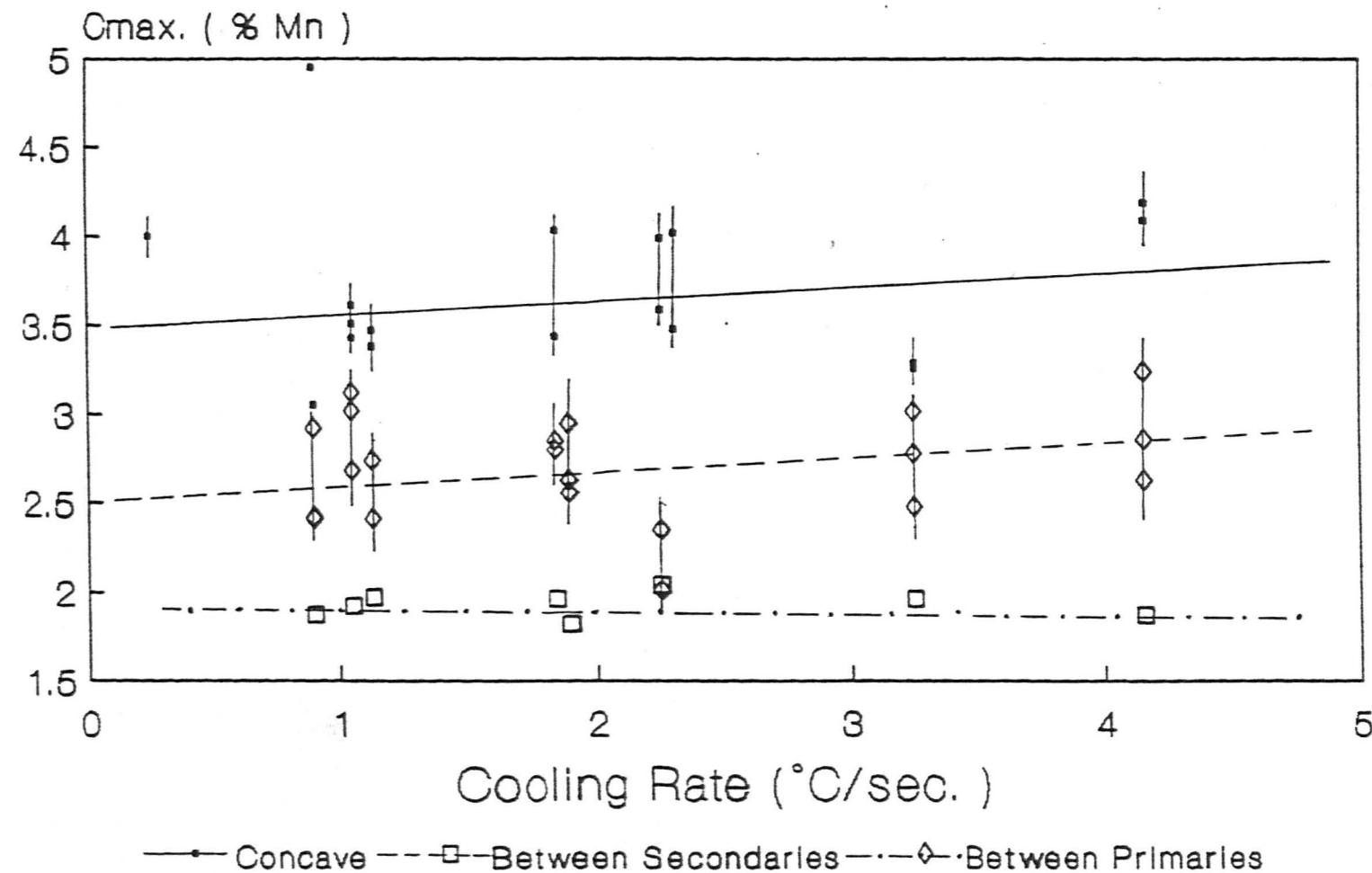
0.8 % C - 1.6 % Mn - Fe



1200°C

Figure 83

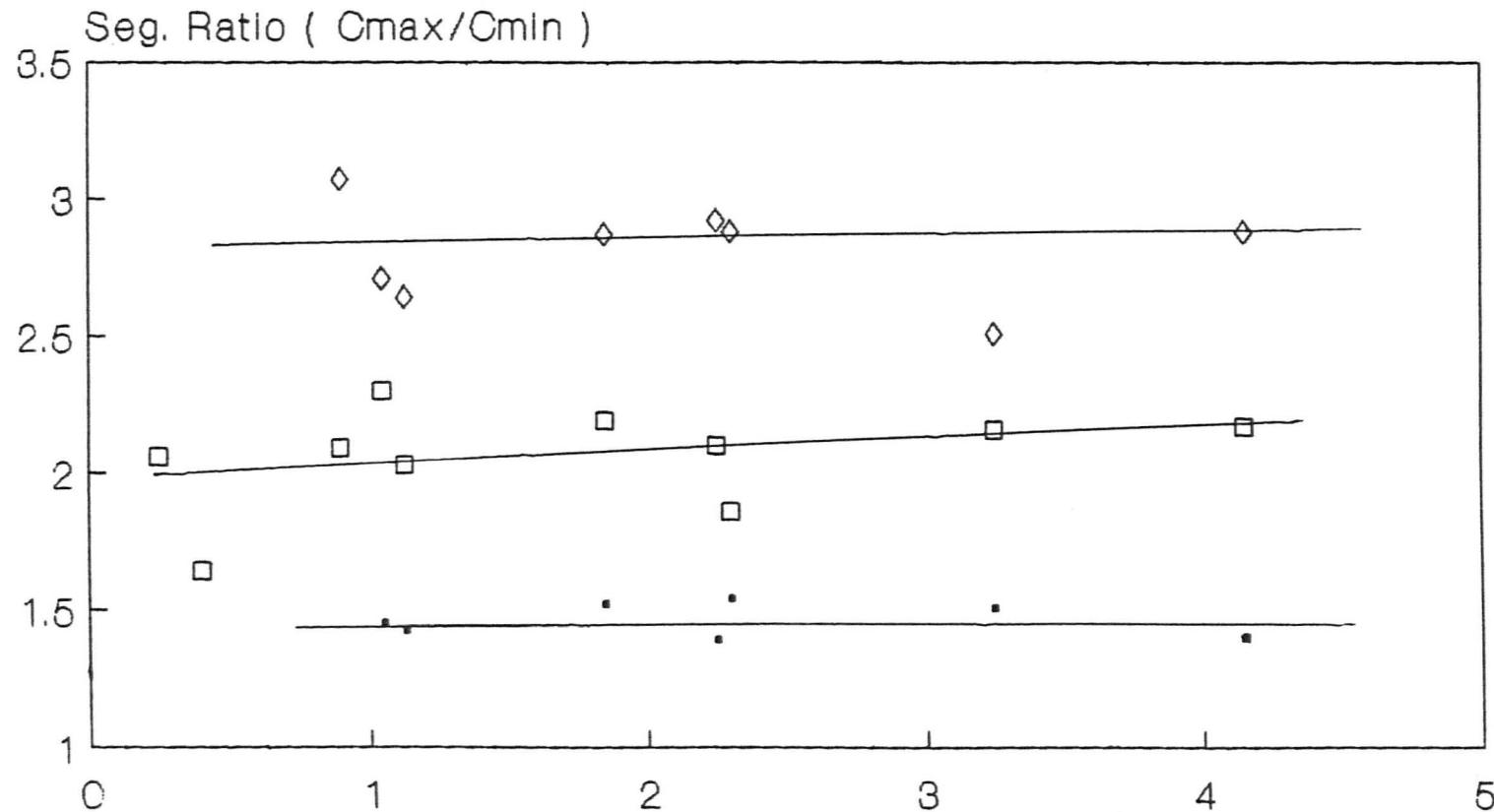
The maximum concentration of manganese as a function of cooling rate for concave solidification points by comparing between primaries and secondaries



0.8 % C - 1200 °C

Figure 84

The segregation ratio for concave solidification points by comparing secondaries and primaries



• Between Secondary □ Between Primary ◊ Concave

1200°C

Figure 85

**Primary dendrite arm tip shows the beginning of segregation of
manganese for 0.8 % C - 1.6 % Mn - Fe at 1.5 mm/min growth rate
(mag. X 205)**

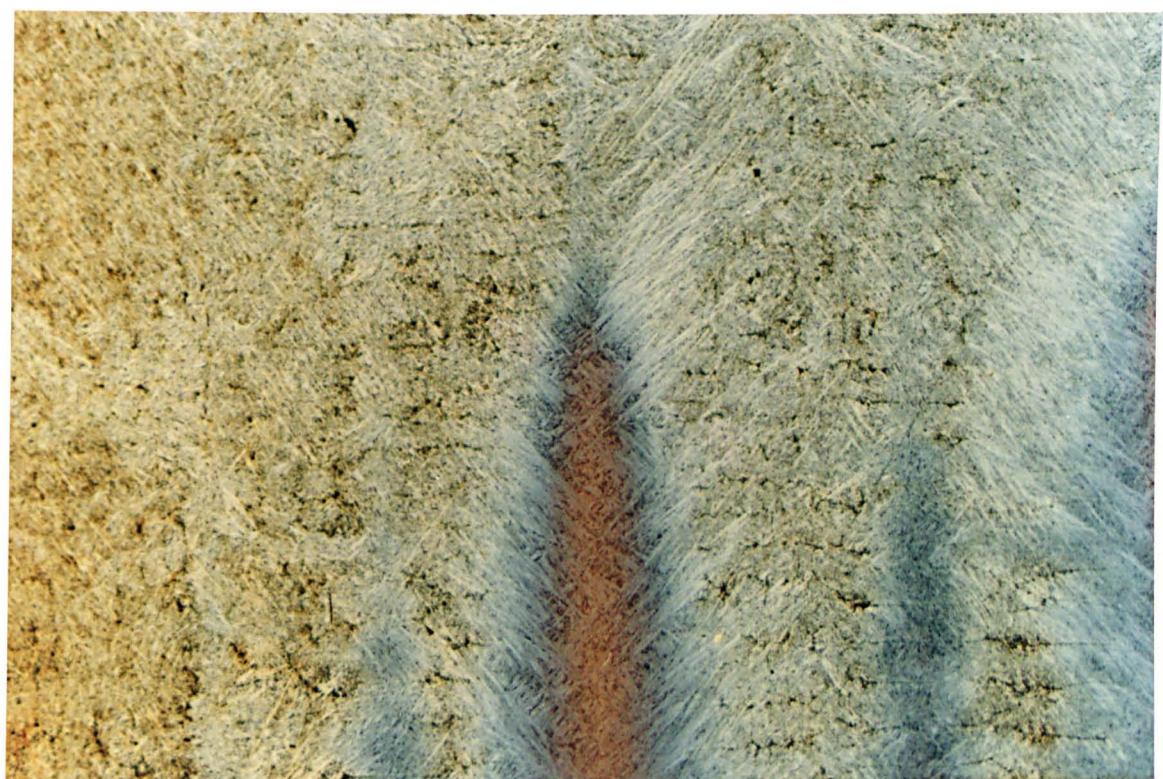


Figure 86

**Electron micro probe concentration profile through the centre
of primary dendrite tips as shown in the figure 85**

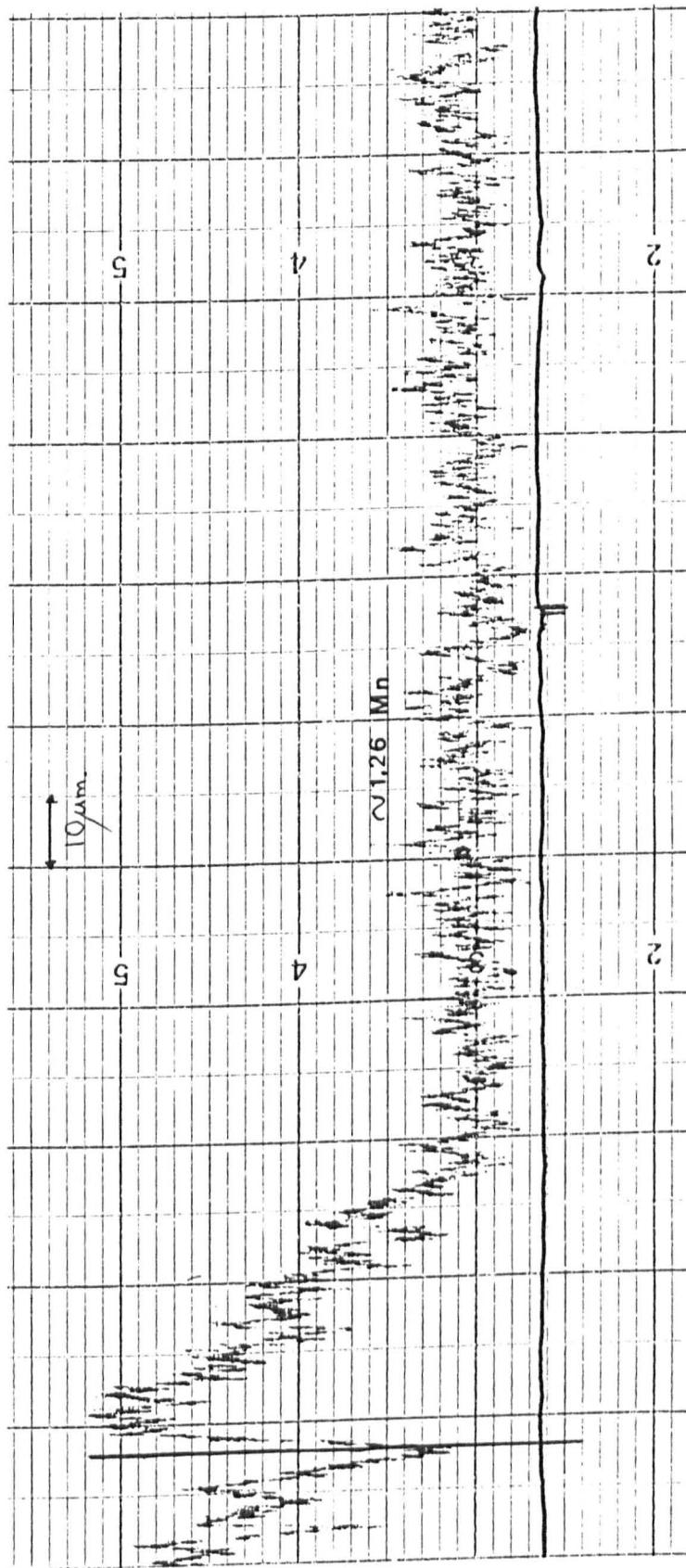
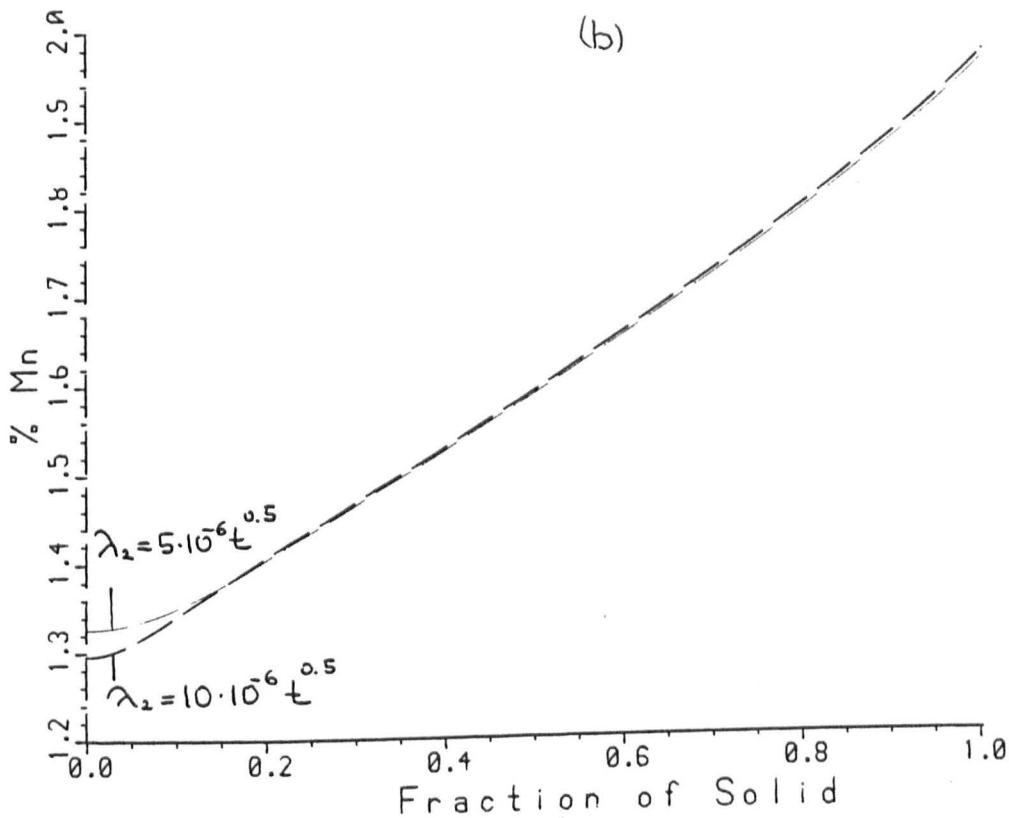
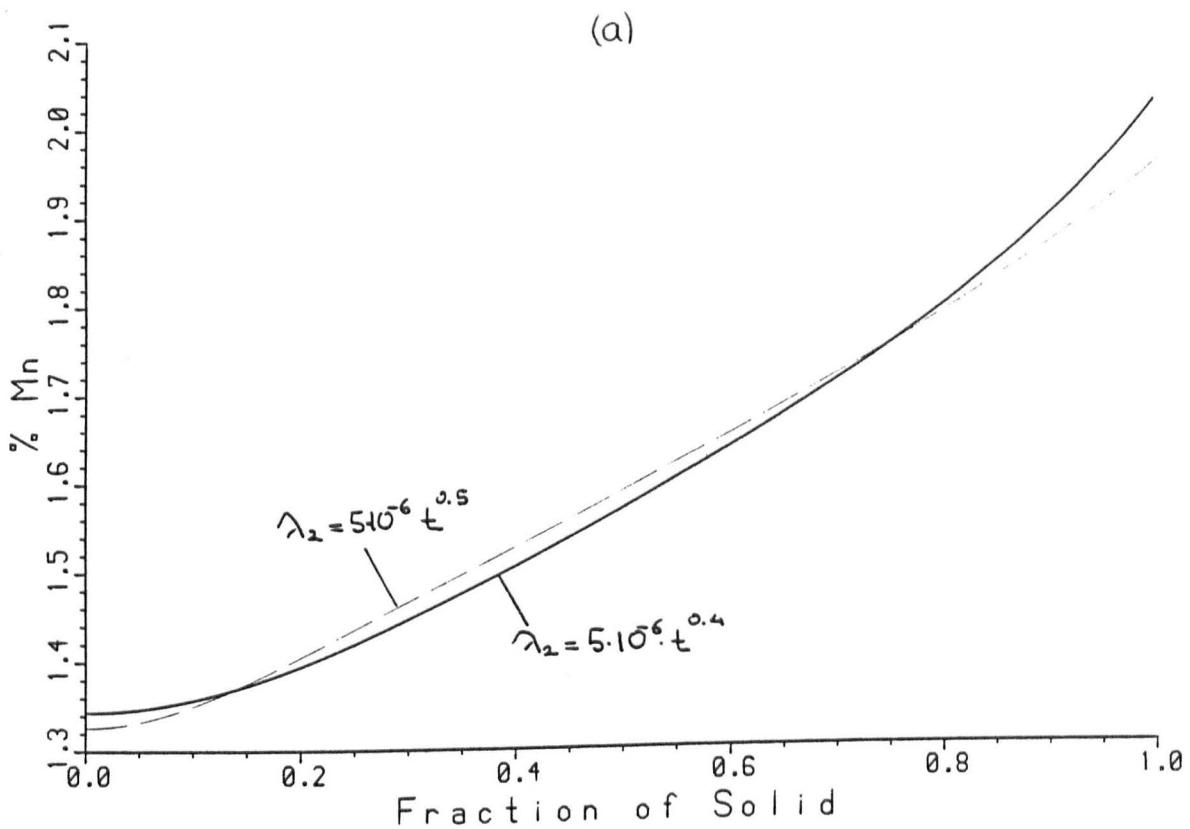


Figure 87

The effect of model variables in secondary arm coarsening model

- a) effect of coarsening equation exponent
- b) effect of coarsening equation pre-exponent
- c) effect of diffusion coefficient
- d) a comparison between dendrite arm coarsening model and constant arm model



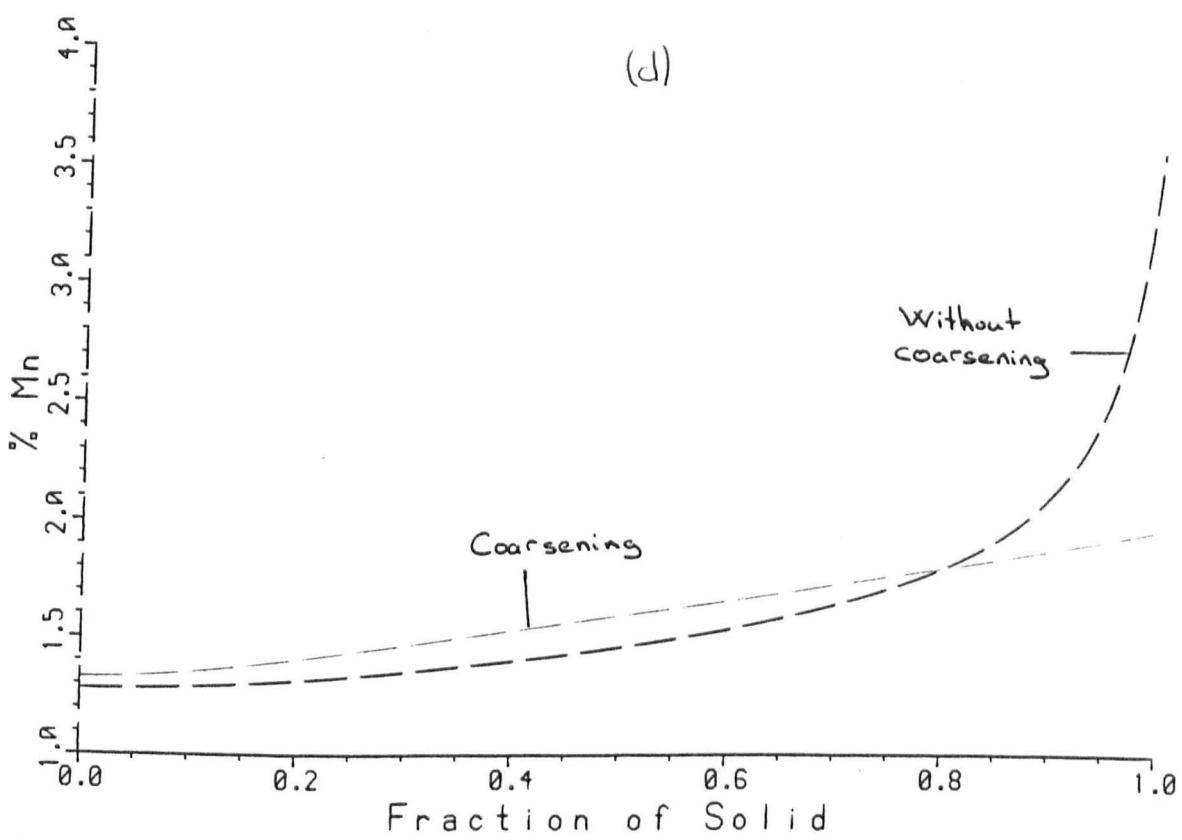
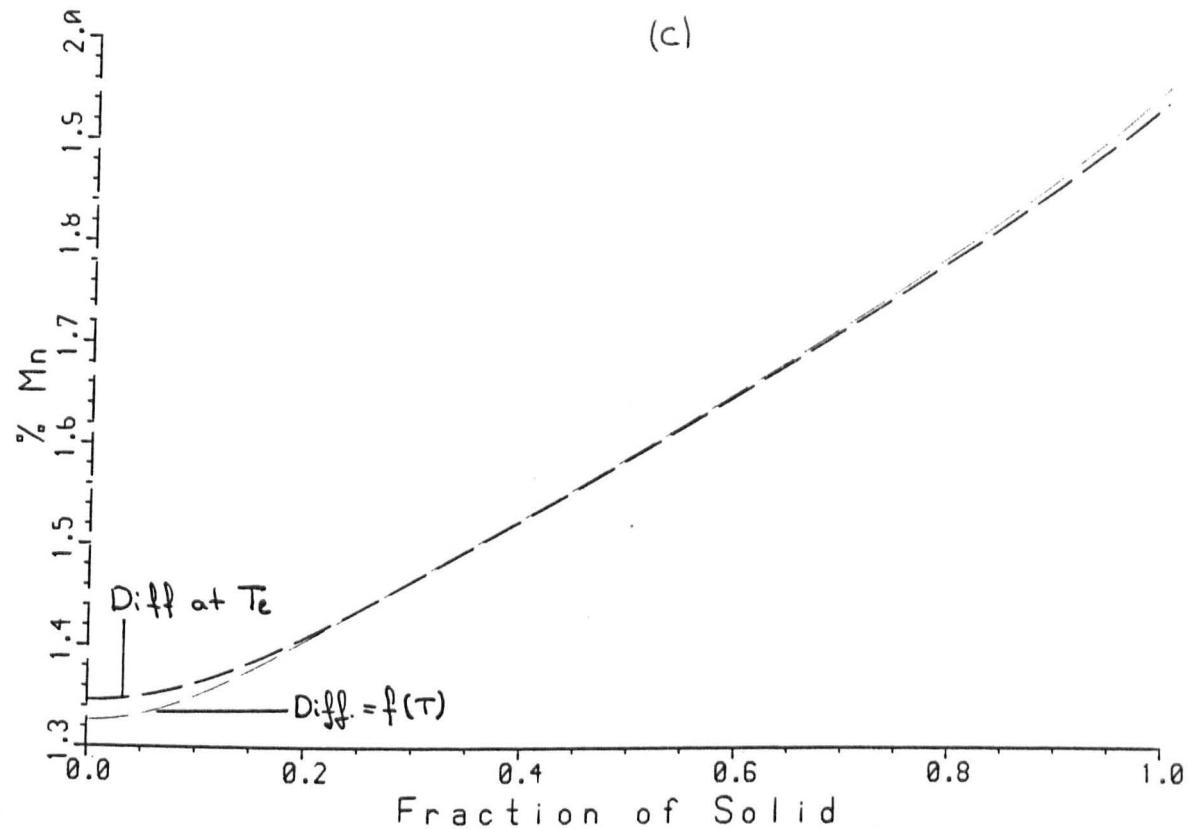


Figure 88

**Secondary arm coarsening computer model prediction for 0.1 % C
at the end of solidification for different coarsening rate**

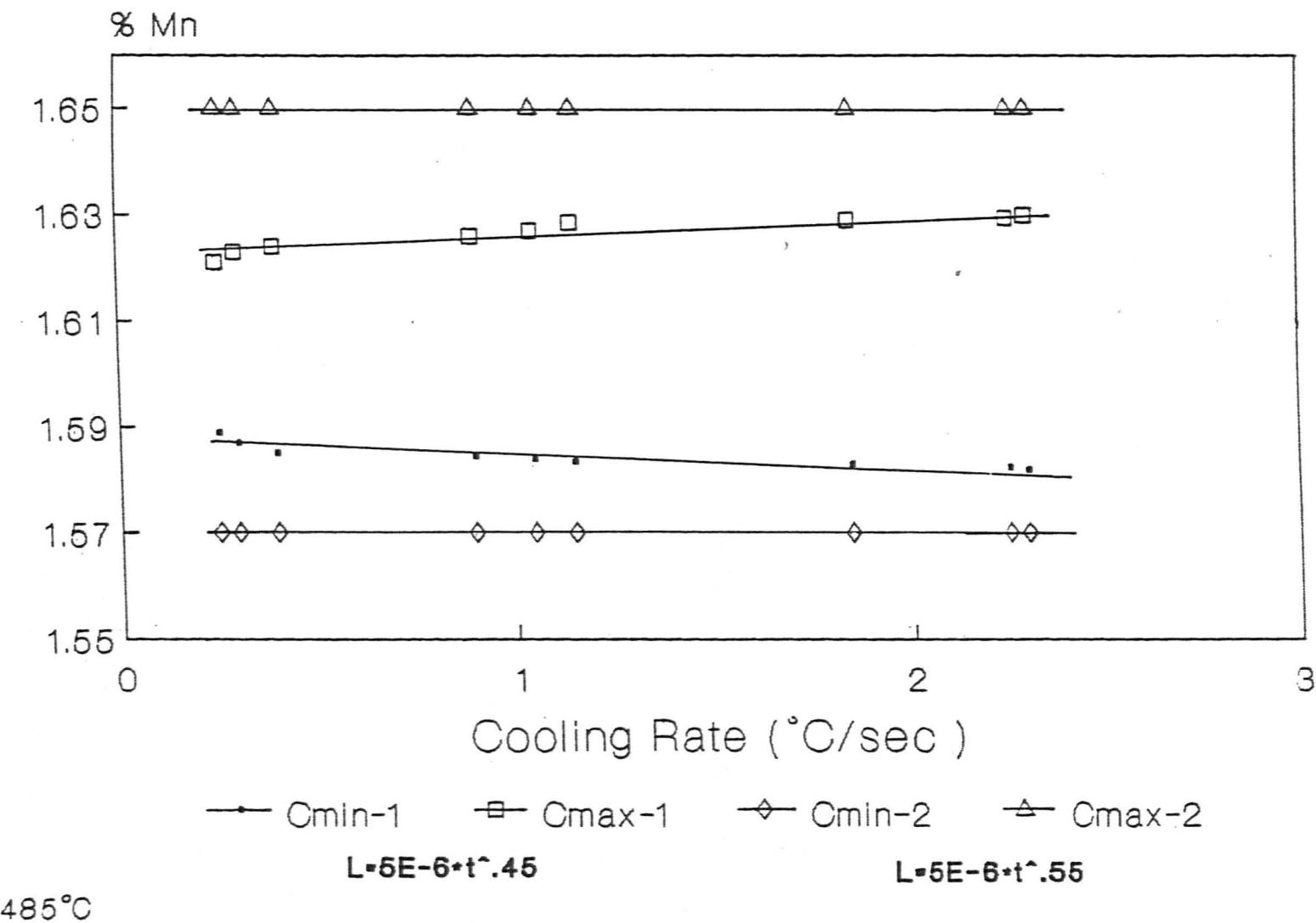
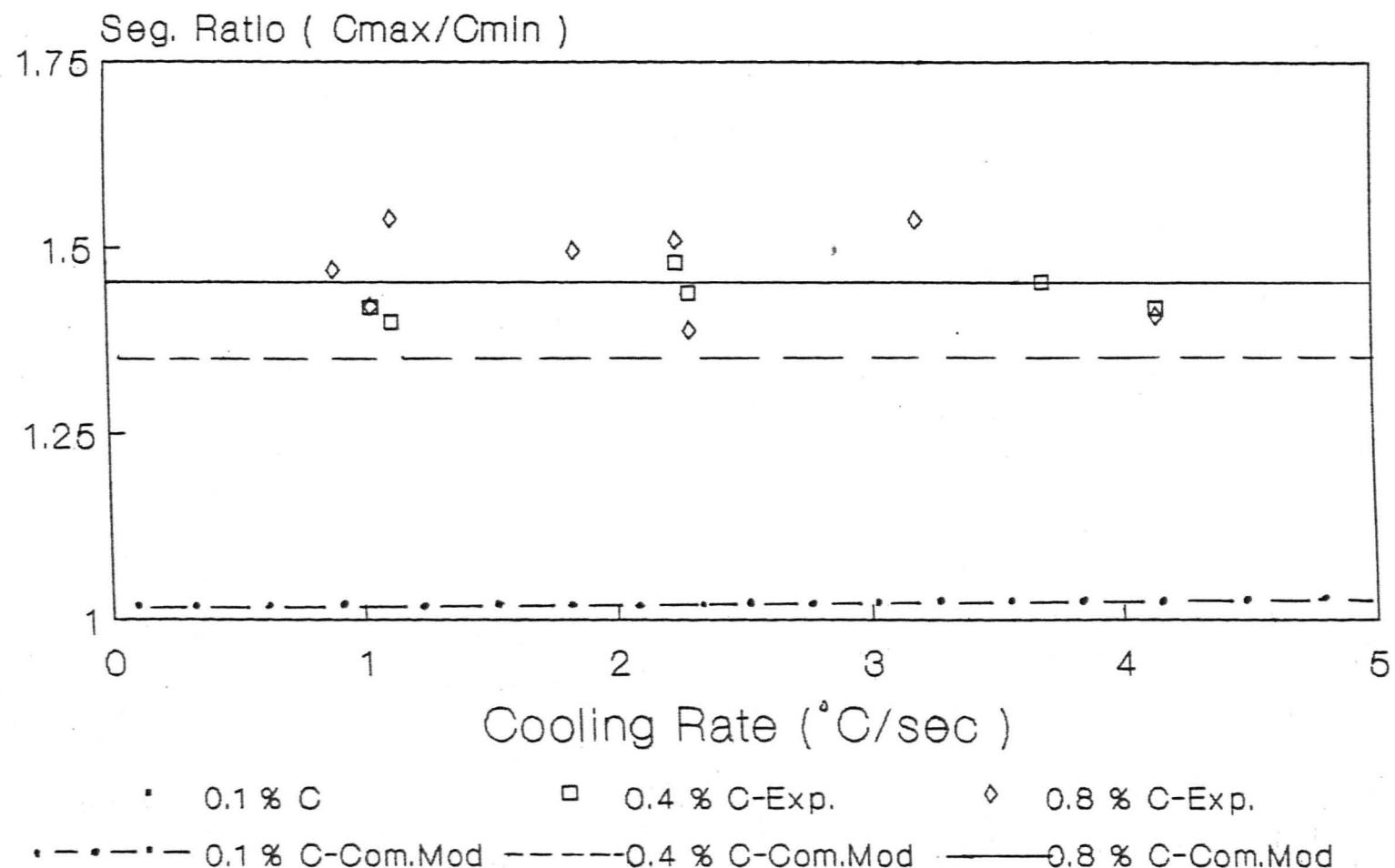


Figure 89

**Comparison of predicted segregation ratio for 0.1 % C at 1485 C
and 0.4 % C and 0.8 % C at 1200 C with experimental results**

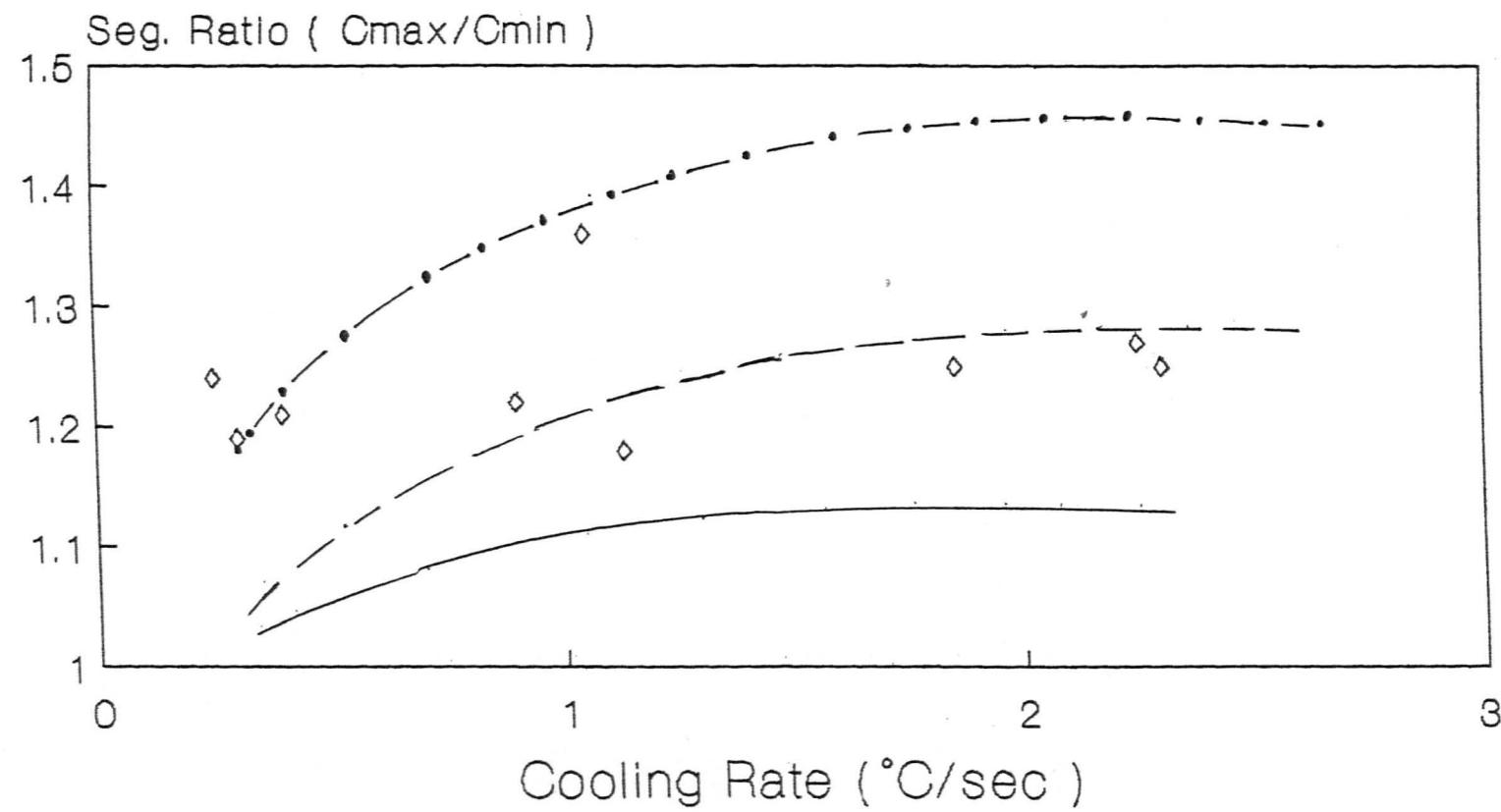


1200°C

Comparison of predicted segregation ratio and minimum concentration of manganese of 0.1 at 1485 C for different morphology of primary arms with experimental results

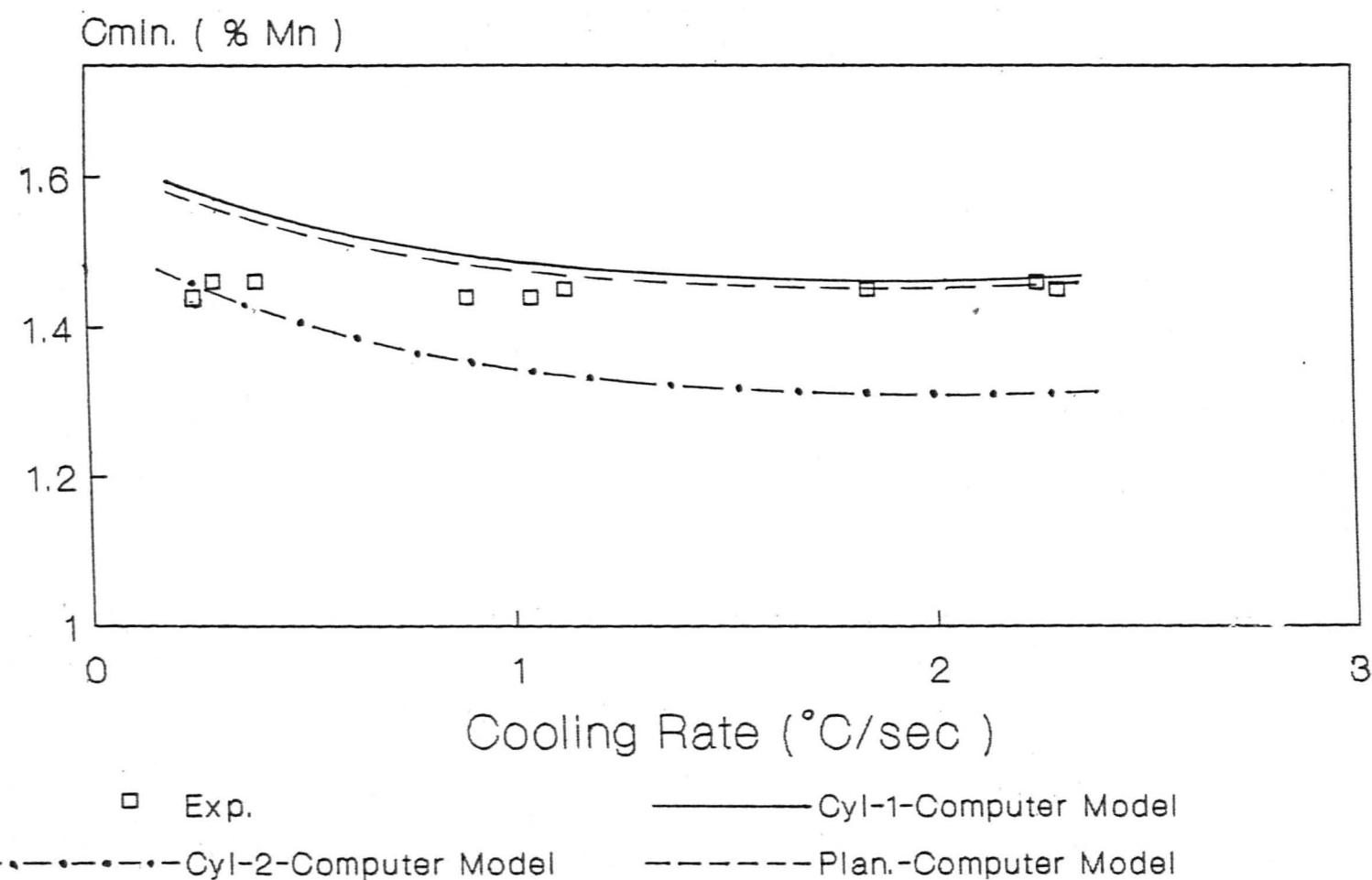
Figure 90 Seg. Ratio

Figure 91 Cmin.



◊ Exp.
—●—●—● Cyl-1-Computer Model
—□—□—□ Plan.-Computer Model

1485 °C - 0.1 % C

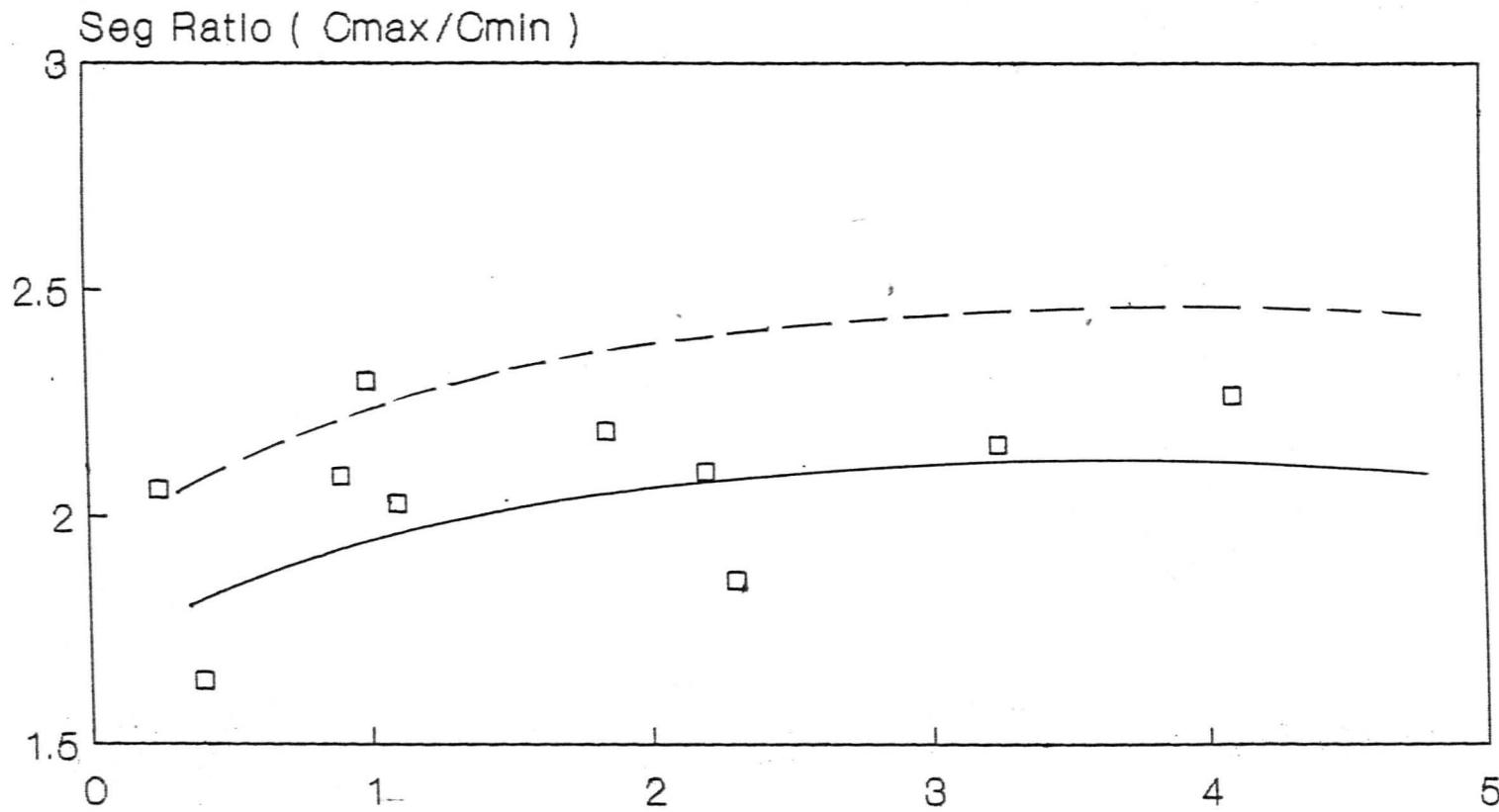


1485 $^{\circ}\text{C}$ - 0.1 % C

Comparison of predicted segregation ratio of different models
for 0.4 % C and 0.8 % C at 1200 C with experimental results

Figure 92 for 0.8 % C

Figure 93 for 0.4 % C



□ Exp. —●— Cyl.-Computer Model - - - - - Plan.-Computer Model

1200°C - 0.8 % C

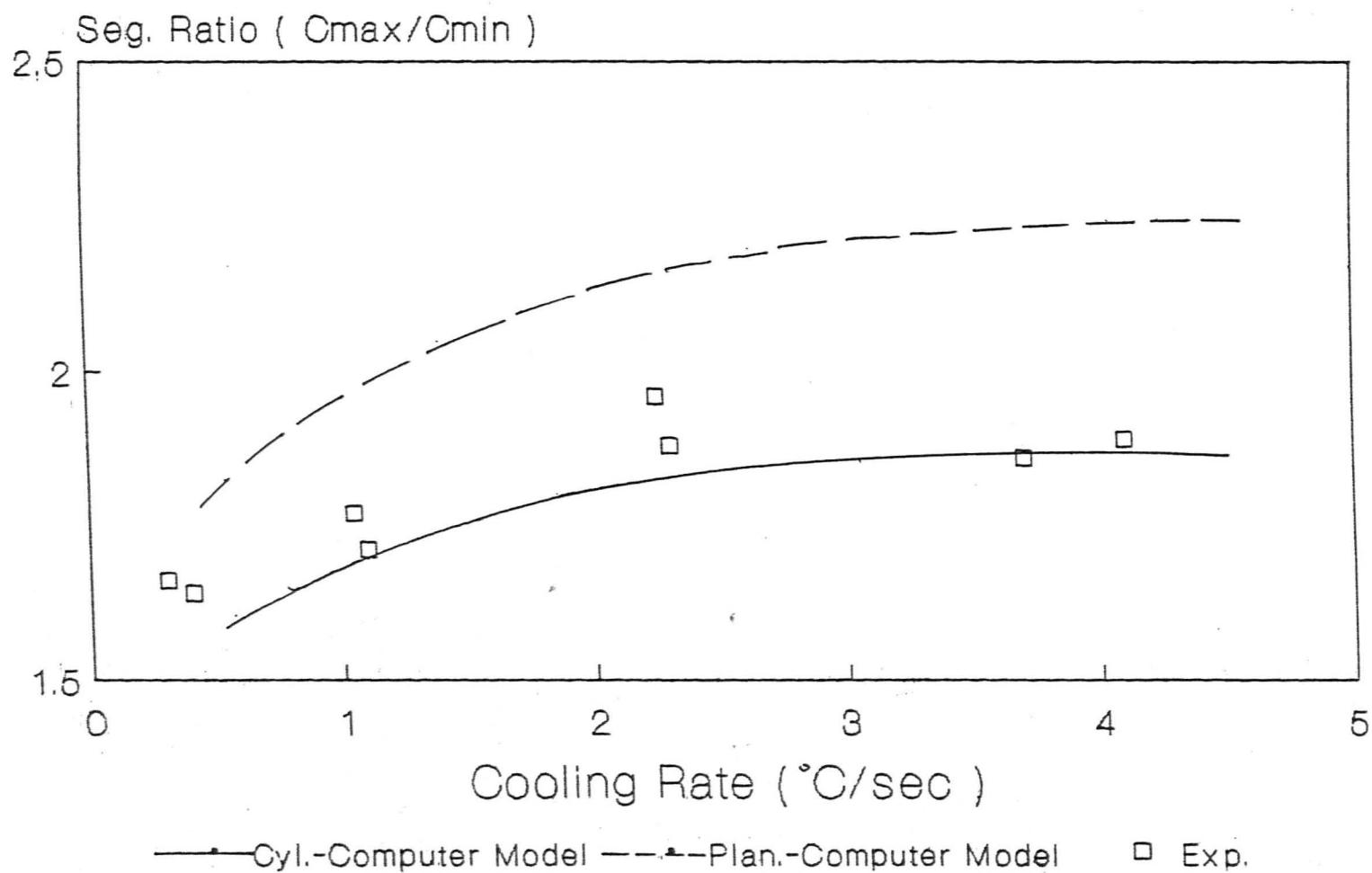
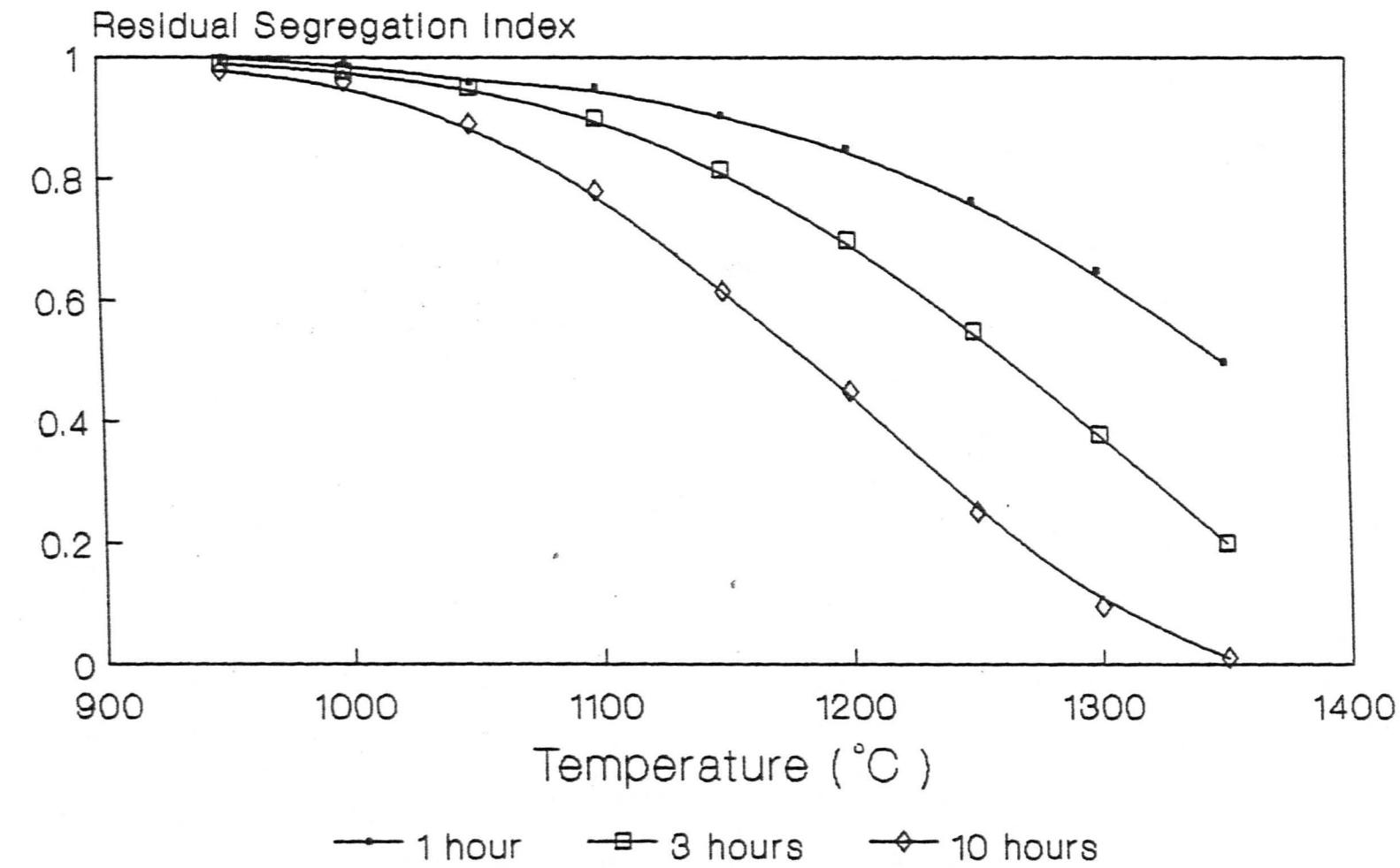


Figure 94

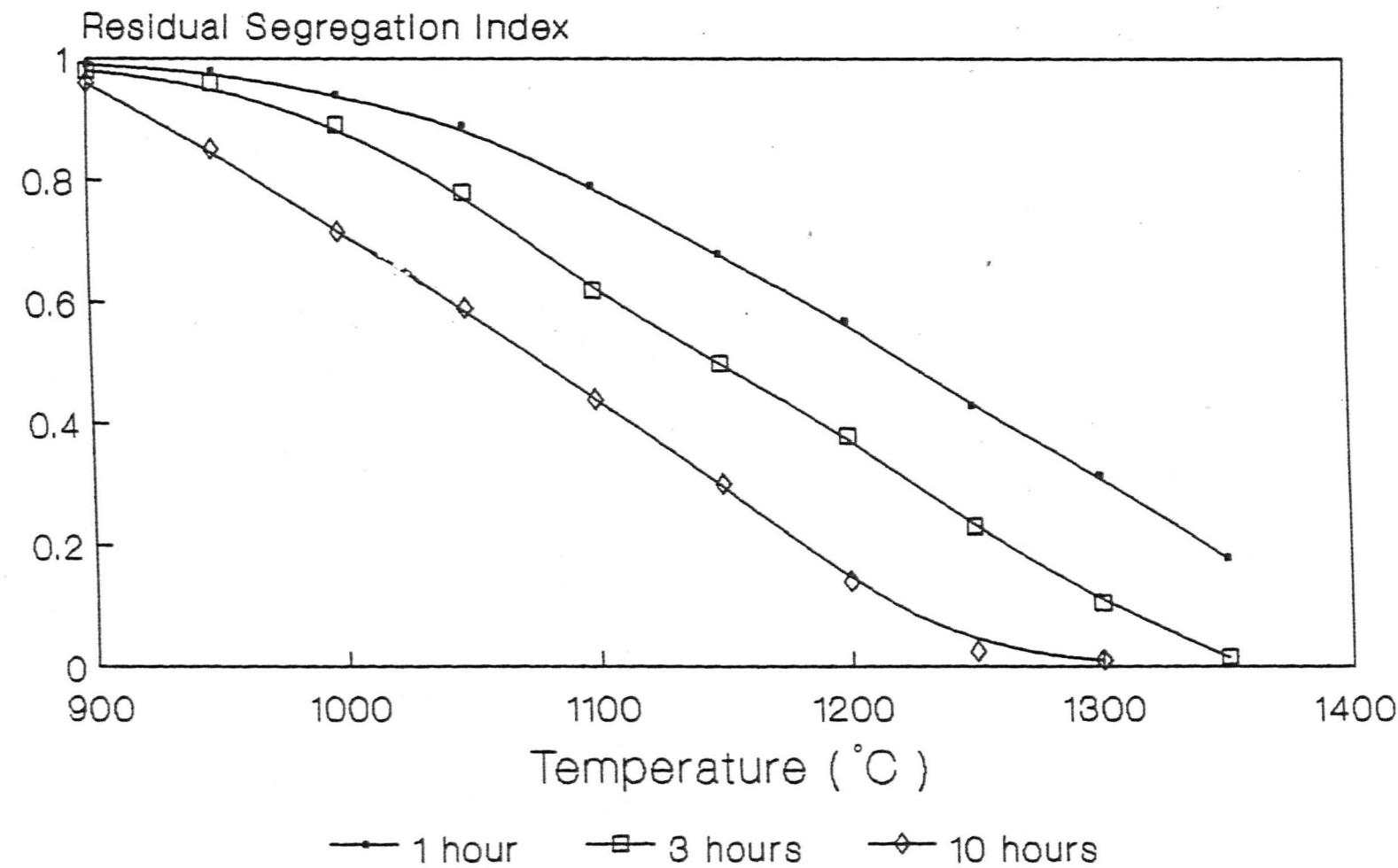
The residual segregation index as a function of temperature and time for 0.4 % C - 1.6 % C - Fe at the highest and lowest cooling rates

a) 0.30 C/sec - 0.4 % C

b) 4.15 C/sec - 0.4 % C



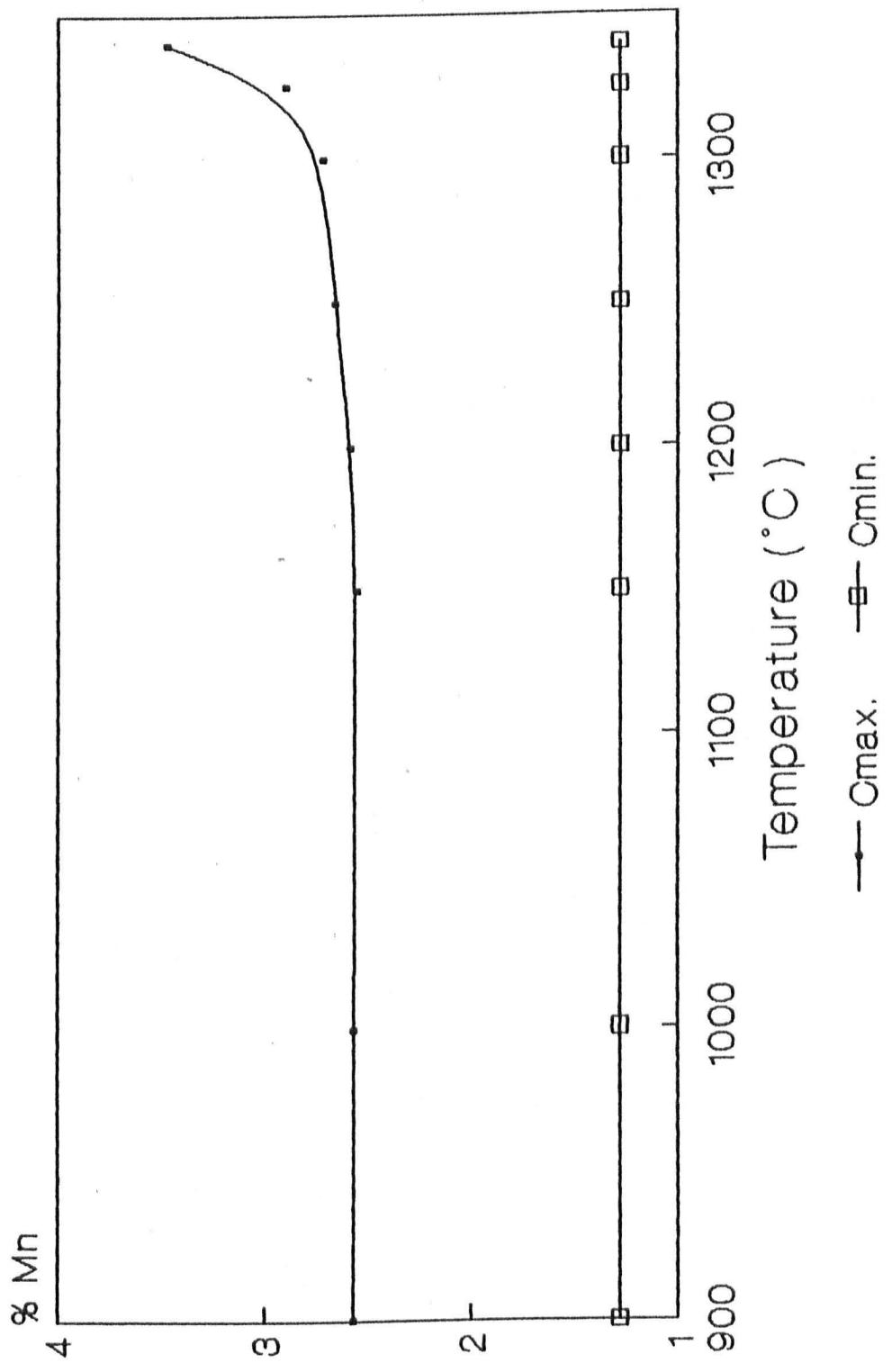
Cooling Rate 0.30°C/sec - $0.4\% \text{ C}$



Cooling Rate 4.15 °C/sec - 0.4 % C

Figure 95

The change in the maximum and minimum concentration of manganese as a function of temperature during the solid state cooling at the 1.5 mm/min growth rate (0.25 C/sec cooling rate) for 0.8 % C



Cooling Rate 0.25 °C/sec. - 0.8 % C

Figure 96

Average segregation ratio as a function of carbon content for
primary arms and secondary arms

