Coupled Growth of a Binary non-facetted/non-facetted Peritectic Organic Alloy

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Abstract

The two organic substances NPG (Neopentylglycol) and TRIS (Tris(hydroxymethyl)aminoethan) are known to have a peritectic phase diagram with a non-facetted/non-facetted region. Between real solid and real liquid the molecules of such organic substances are free to rotate although they are still fixed on their lattice position. This circumstance is the reason that organic substances show the same solidification behaviour as metals do. Therefore, they are quite attractive for in-situ solidification observations in metallurgy since they have rather low melting points. NPG has already been used for this kind of research for a long time and its chemical as well as physical properties are well known. However, TRIS is used the first time for in-situ observations of solidification and its properties are not well defined. So far, two binary non-facetted/non-facetted phase diagrams are known which show a suitable peritectic reaction for in-situ observation. In the presented study investigations on the binary phase diagram of TRIS and NPG are presented. The growth behaviour for the three different regions of the phase diagram was investigated, namely for (i) the hypoperitectic region, (ii) the hyperperitectic region, and (iii) the peritectic region. Several alloys were investigated with a Bridgman furnace and the experimental observations of the solidification structure are discussed for different pulling rates. (i) In the hypoperitectic region, and (ii) in the hyperperitectic region only the primary phase was observed. (iii) The investigations in the peritectic region show at constant low G/V (G temperature gradient, V solidification velocity) that only one phase solidifies and no peritectic reaction was observed. With higher G/V ratio, the solid/liquid interface oscillates between dendrites and cells where both phases are simultaneously present. With high G/V ratio, a banded solidification structure is predicted. Investigations show, that in this region a planar front always consists of just one phase. This could be a consequence of convection occurring ahead of the solidification front. Different solidification behaviour was observed after a quick change of the pulling rate. The high G/V ratio was changed for a short time to a low G/V rate and then back to the original G/V ratio. In this case, dendrites in the hypoperitectic region (i) transform to cells whereby the dendrite surface and the secondary arms strip off and move against the pulling direction. This could be a consequence of the fact that the secondary phase nucleated on the surface of the primary dendritic phase. Further more, coupled growth is observed in the peritectic region (iii) where both peritectic phases grow simultaneously in form of cells.

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by
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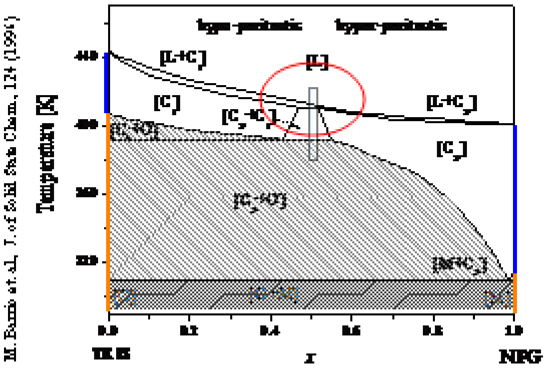
Outline

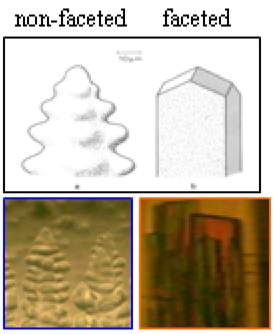
- Introduction
  - Objects and Funding
  - Organic Model System
  - Observation System
- Expected Solidification Morphologies
- Observed Solidification Morphologies
- Discussion and Conclusions

Objects and Funding

- **Objects**
  - Direct optical observation of predicted discrete band formation by diffusive growth of a transparent model with a peritectic reaction.
  - Comparing of results with convection (on earth) and without convection (in space).
  - To deepen the understanding of peritectic reactions especially for Fe and Cu alloys.
- **Funding**
  - 2000: Funding of "*Metastable Solidification of Composites: Novel Peritectic Structures and In-Situ Composites*" (METCOMP) by the European Space Agency (ESA).
  - 2007: Co - funding of our work package by the Austrian Space Agency (ASA).

Organic Model System



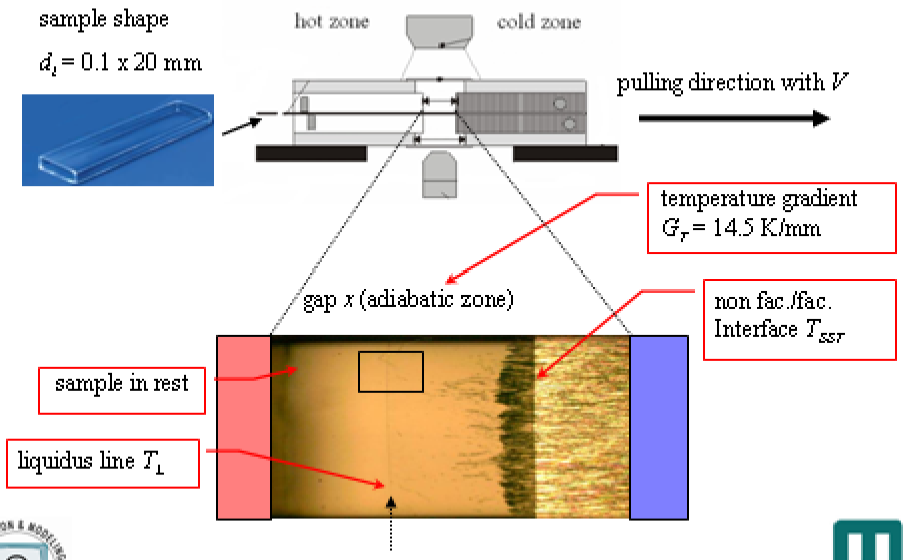


Non optically active phases [C_I] and [C_{II}] (non-faceted)

Optically active phase [M] & [O] and non optically active phase [C_I] & [C_{II}]

Optically active phase [M] and [O] (faceted)

Observation System (Bridgman-furnace)



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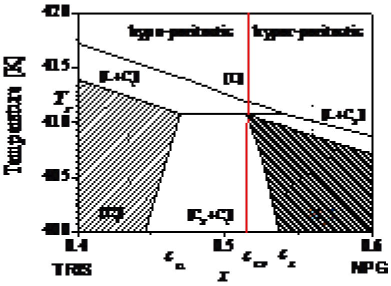
Expected Solidification Morphologies for $V > V_C$



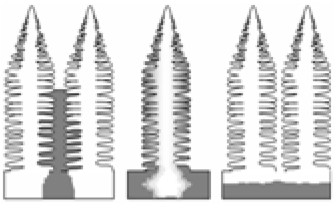
$V > V_C$ cells and/or dendrites

$V < V_C$ planar front growth

V solidification velocity

V_C critical velocity (no constitutional undercooling)

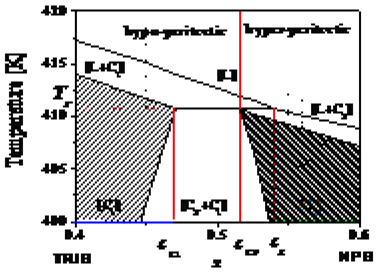
- I: Direct solidification from liquid
- II: Peritectic reaction
- III: Peritectic transformation



I II III

Expected Solidification Morphologies for $V \leq V_C$

[CI]-planar front is stable ($C_o \leq C_{CI}$) and [CF]-planar front is stable ($C_o \geq C_L$)

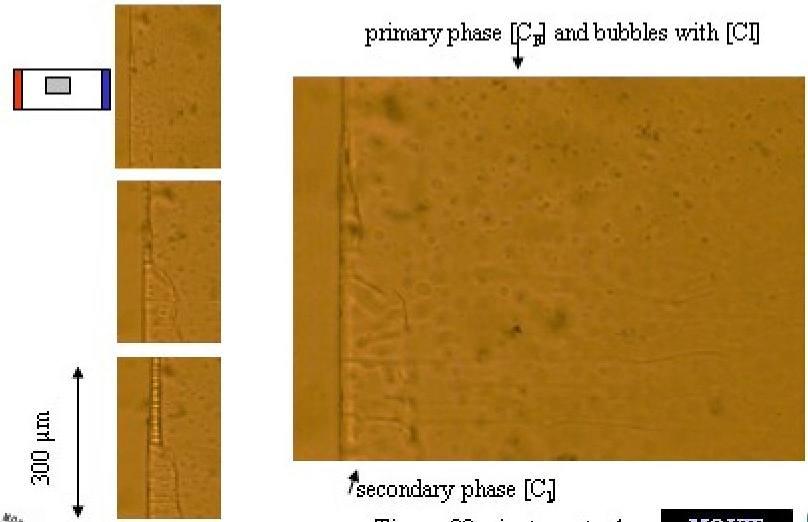


- Non of the planar front is stable, possible band formations ($C_{CI} \geq C_0 \leq C_{CF}$)
- [CF]-planar front is stable but [CI] -phase may nucleate ($C_{CF} \geq C_0 \leq C_L$)

V solidification velocity

V_C critical velocity (no constitutional undercooling)

Investigation for $V = 0$ m/s , $C_0 = 60$ mol.% NPG



Time = 20 minutes $\Delta t = 1$ s **MOVIE**

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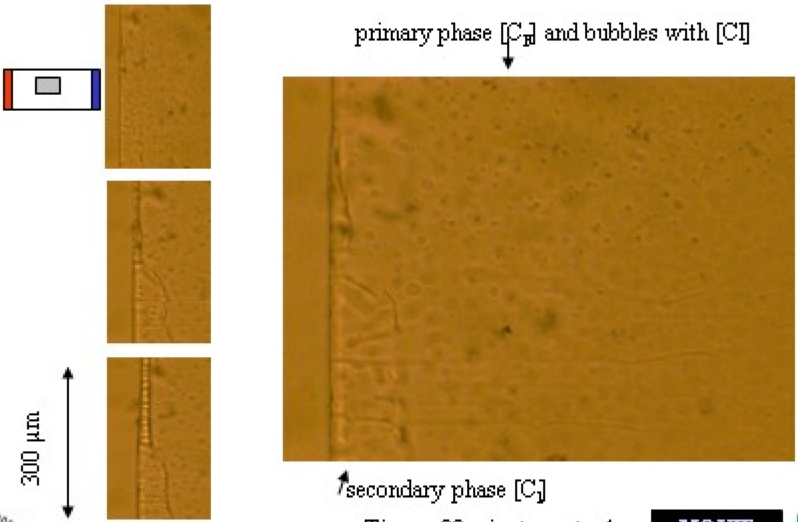
Investigation for $V = 0$ m/s , $C_0 = 60$ mol.% NPG



Time = 20 minutes $\Delta t = 1$ s **MOVIE**

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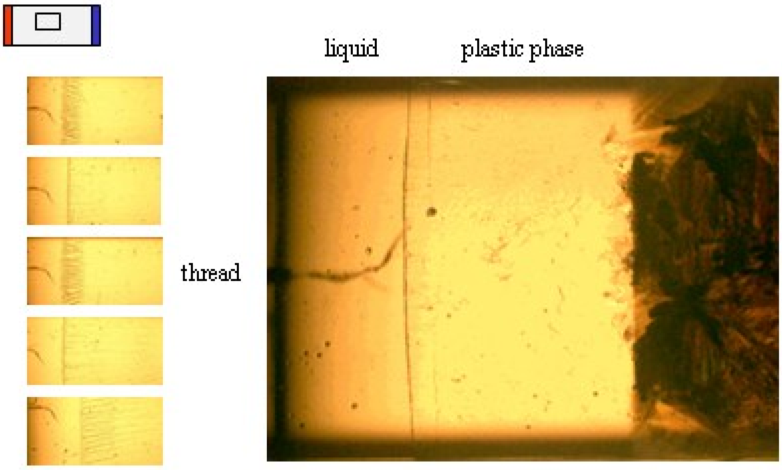
Oscillated Growth for $V > V_C$, $C_0 = 50$ mol.% NPG



solid/liquid interface glass sample

$V = 0.9 \cdot 10^{-6}$ m/s, $G/V = 1.6 \cdot 10^{10}$ K·s/m² Time = 4.5 hours $\Delta t = 30$ s

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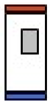
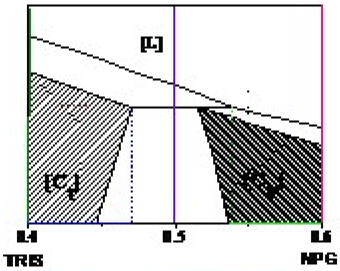
Micro Structure Transformation for $V < V_C$ to $V > V_C$

C_0 = 40 mol.% NPG | C_0 = 50 mol.% NPG | C_0 = 60 mol.% NPG



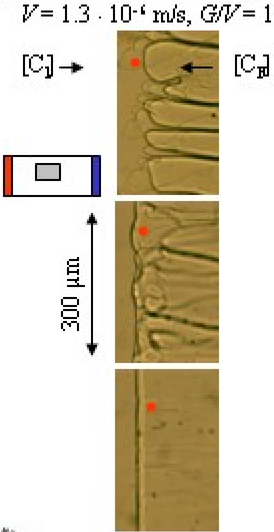


from

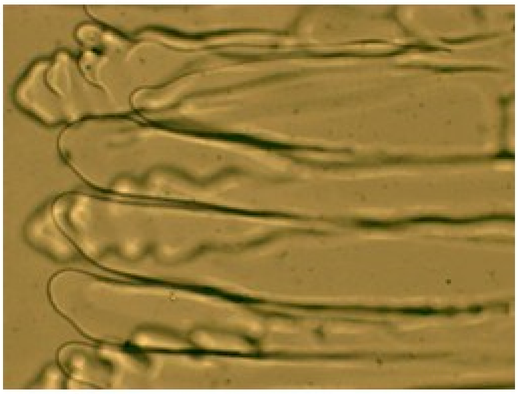
$V = 6.4 \cdot 10^{-8}$ m/s
to
$V = 1.3 \cdot 10^{-6}$ m/s

Coupled Growth for $V > V_C$ to $V < V_C$, C_0 = 50 mol.% NPG

$V = 1.3 \cdot 10^{-6}$ m/s, $G/V = 1.1 \cdot 10^{10}$ K·s/m²



dendrites [C]



cells [C]

Time = 3.7 hours Δt = 30 s

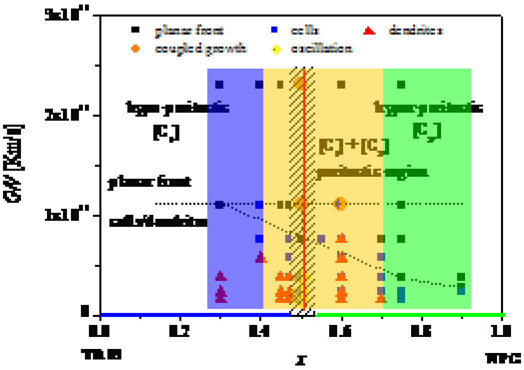
$V = 0.1*10^{-6}$ m/s, $G/V = 1.1 \cdot 10^{11}$ K·s/m²

Outline

Results and Discussion

The solidification morphology shows for the phase diagram TRIS – NPG:

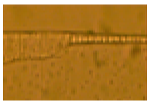
- $C_0 \leq 40$ mol% NPG
  [C_α]- grows
- $C_0 \geq 70$ mol% NPG
  [C_β]- grows
- $40 \leq C_0 \leq 70$ mol% NPG
  second phase can grow
- $C_0 = 50$ mol% NPG
  both phases grow together
  $V \leq V_c$ oscillating
  $V \leq V_c$ as lamellas



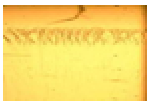
Conclusions

Conclusions

- Hypo-peritectic region, [C_{I}] phase:
  - Dendrites, cells, planar front
- Hyper-peritectic region, [C_{II}] phase:
  - Dendrites, cells, planar front
  - Peritectic reaction for unmoved samples (A)
- Peritectic region, [C_{I}] + [C_{II}] phase:
  - Dendrites, cells, planar front
  - Oscillation (B), coupled growth (C), and
  - peritectic reaction for unmoved samples



A



B

C

Limitation

- Small decomposition of TRIS for long time investigations
- Narrow region which shows a peritectic reaction

Thank you for your attention!

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