

## Recurring instability of cellular growth in a near peritectic transparent NPG-TRIS alloy system

A. Ludwig<sup>1,a</sup>, J. Mogeritsch<sup>1,b</sup>

<sup>1</sup>Montanuniversitaet Leoben, Department of Metallurgy, 8700 Leoben, Austria

<sup>a</sup>ludwig@unileoben.ac.at, <sup>b</sup>johann.mogeritsch@unileoben.ac.at

**Keywords:** Directional solidification, cellular growth, peritectic system, recurring instability

**Abstract.** In this study, a near peritectic transparent metal-like solidifying NPG-TRIS alloy was directionally solidified in a thin sample under process conditions which favor cellular growth. Different to an identical horizontally processed sample, the vertically processed sample revealed a cellular array which was curved. This curving was attributed to a convection-induced higher alloy concentration at the sample edges compared to the sample center. Surprisingly, it was found that the curved cellular array is inherently unstable as three times dendrite-like structures shot forwards. As origin of these rapid advancements two possibilities were discussed. Either a convection-induced variation of the solute boundary layer might be responsible. Or it can be explained by a more generic approach which due to the curved form of the cellular array considers extended freedom for cellular branching in combination with a relative large deviation of the preferential crystal growth direction from the heat flow direction. For the discussed phenomena the presence of the peritectic phase within the intercellular spacing was found to be not of importance.

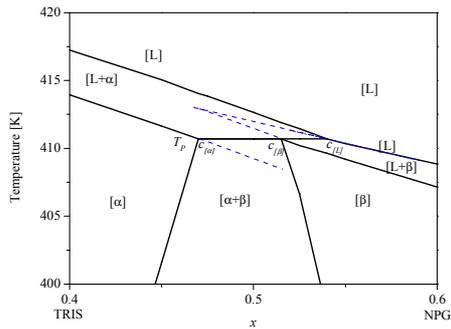
### Introduction

Direct solidification of transparent metal-like solidifying model substances in a micro Bridgman-furnace [1, 2] enables in-situ observations of the dynamics of the solid/liquid interface morphology [3]. In order to observe the pure diffusion-driven morphology evolution, convection in the sample should be avoided. This is why often very thin samples are processed either horizontally or vertically. In case that the solute boundary layer associated with the growth morphology reveals a lower density compared to the bulk melt, vertically processed samples might show a higher risk of natural convection to occur. The question of the degree of convection becomes especially important when near peritectic alloys are solidified close to the limit of constitutional undercooling. Here, the solidification rate is so small that even a slight motion of liquid might affect the appearance of different morphologies. For metallic near-peritectic alloys various morphologies like bands, islands, and isothermal peritectic coupled growth were found [4, 5, 6]. Ludwig and Mogeritsch [7, 8] performed investigations of the solid/liquid interface dynamics with organic near-peritectic model substances and reported additionally a competitive oscillation growth between the primary and the peritectic phase.

The motivation for the present study was to change the degree of convection which occurs during solidification of near-peritectic transparent NPG-TRIS alloys in thin samples by changing from horizontal to vertical growth direction and keeping all other parameters constant.

### Experimental procedure

A peritectic reaction is characterized by the formation of the peritectic  $[\beta]$  phase from the primary  $[\alpha]$  phase and the liquid  $[L]$  at the peritectic temperature,  $T_p$ , and the peritectic concentration,  $C_{[\beta]}$  [9]. The binary phase diagram of the organic compounds TRIS (Tris(hydroxyl-methyl)amino-methane) - NPG (Neopentylglycol) [10] shows such a peritectic reaction with a peritectic plateau from 0.47 to 0.54 mol fraction NPG and the peritectic concentration at 0.51 mol fraction (Fig. 1). The solid phases which are involved in the peritectic reaction are both non-faceted (also called plastic phases), and therefore solidify similar to metals. As described in [11, 12, 13], close to the peritectic concentration and for solidification conditions where one or both solids tend to grow with a planar interface, the two solids may form a variety of different growth morphologies.



**Fig. 1:** Peritectic region of the binary phase diagram TRIS - NPG. The metastable extension of the liquidus and solidus lines are indicated with blue dotted lines.

brass blocks separated by a 7 mm gap and thermally isolated by ceramic covers, (Fig. 2). The upper brass block served as hot zone and the lower as cold zone, the gap as the adiabatic zone.

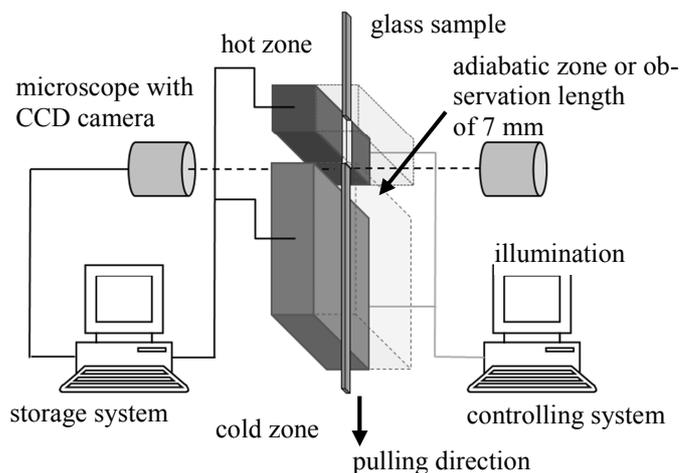
The temperature within the brass parts were controlled by electrical resistant heaters and measured with Pt 100 temperature sensors placed inside each brass block. A  $2.5 \times 0.4 \text{ mm}^2$  slot was milled in the brass blocks to guide the rectangle glass samples. The sample was illuminated through glass windows which were placed in the ceramic covers at the adiabatic zone. Observation of the solid/liquid interface morphology was done with a ZEISS microscope which was equipped with a CCD camera. During the solidification experiments, pictures of the interface morphology were recorded simultaneously with the temperatures of both brass parts. The movement of the glass sample through the furnace was PC-controlled and the corresponding displacements were also recorded.

For the experiments relevant for this publication, a sample with 0.5 mol fraction NPG was put into the preheated micro Bridgman-furnace. For that the furnace was shortly opened and the sample was put into the desired position. So only the segment of the sample close to the hot zone was molten. The pressure increase which might be caused by the expansion on heating and melting was released by the fact that a solid material column at room temperature does not fill the tube completely. The low temperature faceted phases, which are stable at room temperature, reveal 10-20% higher densities compared with the high temperature plastic phases and while cooling of the just filled sampled the contraction of the faceted phases opened up visible gaps and cracks. So the heated and finally molten segment can easily push the solid segments above and below aside and a pressure-free molten segment can form.

After the positioning, the sample was held in rest for 60 minutes to establish a thermal equilibrated state. During this time the solid/liquid interface in the adiabatic zone became microscopic and macroscopic planar. Afterwards, the sample was pulled with a constant pulling rate of  $V_p = 0.16 \text{ }\mu\text{m/s}$  through the furnace and the storage system was started to record pictures and tem-

The organic compounds TRIS and NPG [14, 15, 16] are common industrial products. Both highly hydroscopic [17] compounds were delivered as powder from Adrich [18] with an indicated high purity of 99.9+% for TRIS and 99% for NPG. An additional treatment process for NPG was used to reduce the water content and thus increase the purity. Alloys were prepared by mixing the powders of both organic substances and fusing them together. Thin rectangle glass samples ( $0.1 \times 2 \text{ mm}^2$  inner cross section with  $100 \text{ }\mu\text{m}$  wall thickness [19]) were filled by capillary force and sealed with glue. All operations for filling were done in an Argon atmosphere within a glove box.

The micro Bridgman-furnace was made of two



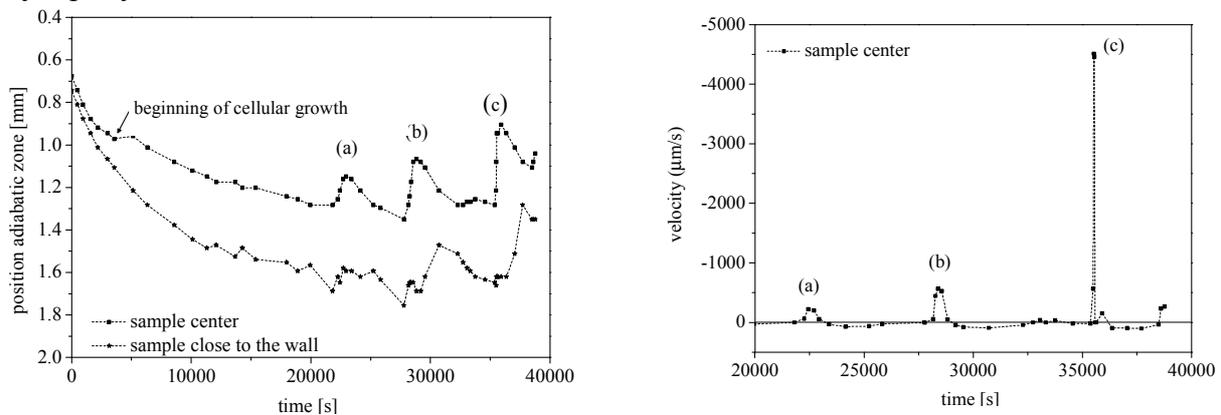
**Fig. 2:** Sketch of the micro Bridgman-furnace. From the hot and the cold zone only the rear half is depicted. The molten section of the alloy within the hot zone and within the adiabatic gap is shown transparent.

peratures with a timeframe of 30s. After approximately 12 hours the sample's end reached the hot zone and the experiment was stopped. For the unmoved as well as the moved sample, we have estimated and validated at the position of the solid/liquid interface a constant temperature gradient of  $G_T = 6.5 \text{ K/mm}$ .

## Results

During solidification the initial planar solid/liquid interface changed to shallow cells and then to deep cells. While changing the morphology, the envelope of the solid/liquid interface curved more and more until it reached after 3 hours a constant shape. Additionally, the solid/liquid interface recoiled for approximately 5 hours. Within the intercellular liquid, solidification of the peritectic phase was visible. After 6 hours the solidification morphology in the middle of the sample changed within minutes to dendrite-like objects and then back to cellular-like. This rapid advancing of dendrite-like objects was observed 3 times and at each cycle the dendritic tips grew faster and more closely towards the hot zone.

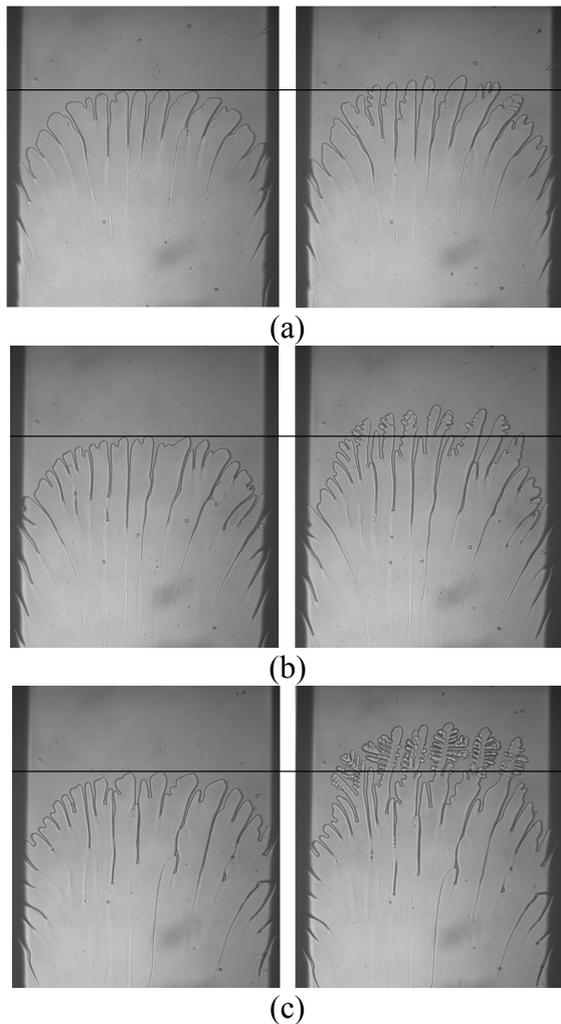
In Fig. 3 the position of the envelope at the sample center and at a point close to the left resp. right wall is shown as function of time. Both, envelope curving and recoiling are obvious. The rapid advancements in the second half of the experiment are labelled by (a)-(c). In the second diagram of Fig. 3, the envelope velocity at the sample center for these three rapid advancements (a)-(c) is shown as function of time. Note that with a "zero" velocity the envelope of the solid/liquid interface does not move relative to the observation window, which means that the growth velocity is exactly equal to the pulling rate. Positive velocities occur when the grow velocity is faster than the pulling rate and negative velocities vice versa. Note also that after the rapid advancements the growth velocity rapidly decreases to and even below zero.



**Fig. 3.** Position of the envelope of the solid/liquid interface at the sample center and close to the sample wall (left) and envelope velocity at the sample center as function of time for the second half of the experiment (right).

In Fig. 4 the morphological changes for the three rapid advancements (a)-(c) are shown. Left pictures are taken shortly before rapid advancement (at local minima of upper curve in Fig. 3 (left)) and right pictures shortly after (at local maxima of upper curve in Fig. 3 (left)). Note that the rapid advancing objects increased their shooting forward distance and became more and more dendrite-like. In Fig. 4(c) the objects which have shot forwards developed clear sidearms with a fourfold symmetry, whereas in Fig. 4(a) they look more like two dimensional parabolic dendrite tips.

Also the respective cellular starting arrays became more and more irregular. In Fig. 4(a) a more or less clear deep cell array is visible, whereas in Fig. 4(c) the array is obviously transient with a spacing which allows secondary branches to develop. Note further that the cell tips reveal a slightly faceted appearance which is more obvious for the cells from which the rapid advancement (c) originated compared to those for (a).



**Fig 4:** Solid/liquid interface morphology before and after the rapid advancements (a)-(c). Each picture shows the 2000 $\mu\text{m}$  wide sample. The dark shadows left and right are caused by the internal curvature of the glass sample. The black lines were added to more easily recognize the distance the dendritic-like objects have shot forward.

observed indication for convection, namely occasionally small dust particle moving downwards at the sample center and upwards at the sample edges (and sideways along the interface in between). The origin of this convection pattern can be discussed as follows. According to the phase diagram (Fig. 1), solidification of a 0.5 mol fraction NPG-TRIS alloy is accompanied by a rejection of NPG at the solid-liquid interface and so a NPG rich boundary layer forms at the cellular array. As NPG is lighter compared to TRIS, a NPG enrichment leads to a density decrease. Although the thermal gradient might suggest a stable density stratification, this solutal density decrease overbalance the thermal density increase and so the NPG boundary layer associated with the solidifying cellular solid/liquid interface gets inherently unstable. This unstable density stratification is finally the reason for the formation of the observed convection pattern. It is obvious that the descending flow at the center which then flow parallel to the macroscopic interface and ascends at the sample edges slightly reduces NPG at the center and enriches NPG at the sample sides. A higher NPG concentration results in a lowering of the corresponding liquidus temperature and thus to a lagging behind of the interface. Therefore, the macroscopic interface curving is caused by segregation differences between sample center and sample edges. This finding is further confirmed by the fact that we have

It is also worth mentioning that after the dendrite-like objects have reached their foremost position they start to thicken and so turned back into a more cellular-like structure which are then the starting cellular pattern for the next rapid advancement. So Fig. 4(b) left has developed from Fig. 4(a) right, and Fig. 4(c) left from Fig. 4(b) right. From Fig. (3) it become obvious that the interface envelope of those starting cellular arrays are approximately at the same position.

### Discussion

In order to identify the growing phases we are referring to the phase diagram given in Fig. 1. For a 0.5 mol fraction NPG alloy it is obvious that the  $[\alpha]$  phase grows at higher tip temperature (higher position) compared to the  $[\beta]$  phase. Therefore, the cellular growing phase is presumed to be the primary  $[\alpha]$  phase and the inter-cellular phase the peritectic  $[\beta]$  phase.

For exactly the same experimental conditions as the one described in this paper but with a horizontally tilted Bridgman furnace, we have found always planar/cellular/dendritic interfaces which were macroscopic straight and perpendicular to the sample axes. Therefore, it can be concluded that the corresponding isotherms are also straight and perpendicular to the sample axes. Now in the vertically solidifying samples the macroscopic interface shape starts to curve when pulling is switched on. This can be attributed either to the formation of segregation differences and/or to a non-uniform cooling, both originated by convection.

It is worth mentioning that we have indeed

found for hyper-peritectic alloys, a higher probability for  $[\beta]$  phase growth at the edges and for  $[\alpha]$  phase growth at the center.

The origin of the recurring rapid advancement of dendrite-like object cannot be finally clarified. One possibility might be that the descending convection at the sample center swept away the NPG boundary layer from the center towards the sides. So the cell tips might undergo a Mullins-Sekerka morphological instability and as consequence dendrite-like structures shot forward and subsequently grow at a higher tip temperature. The swept away NPG accumulates near the two sidewalls, where its accumulation lowers the liquidus temperature (lagging behind of cellular growth). However, beside this accumulation NPG-rich melt (which is lighter) might also ascend along the side wall towards the bulk melt. Depending on the size of the occurring convection rolls the increased NPG concentration might sooner or later return to the sample center where it might lead to a re-establishment of cellular growth.

Another possible origin of the recurring rapid advancement of the dendrite-like objects might be more generic. In a recent paper by Chen et al [20] it is reported, that a transition from cellular to seaweed growth (with or without passing a regime of dendritic growth) might also be accompanied by massive oscillations of the foremost tips of the seaweed structure. The specificity of seaweed growth is that the leading tips repeatedly split into two or more parts that then grow on their own. It is known that such a growth morphology might occur through careful control of heat-flow direction and relative orientation of preferential crystal growth direction.

Although in our experiments no seaweed-like structures were observed, we may still see some parallels. In our experiments the curved cellular array has problems to regularly fill the available space and thus a competition between growth at different directions become locally important. In Fig. 4(c) it can be seen that the preferred growth direction of the dendrite-like rapid forward shooting objects deviates by around  $15^\circ$  from the heat flow direction. However, the cells grow in the heat flow directions but within a changing lateral concentration field. This leads to a slight sideways grow of the cells so that free space opens between the tips which then favors branching and growth into other directions rather than the heat flow directions. This might be a similar scenario as with the seaweed growth.

## Conclusions

The comparison of interface morphologies of identical samples processed in a horizontal and a vertically micro Bridgeman furnace revealed that in the vertically processed sample the alloy concentration became higher at the sample edges compared to the sample center. This led to a curving of the cellular array, with cells which grew in heat flow direction but with a lateral varying liquidus temperature. As the curving is quite strong gradually free space between individual cells opened and the cell tips started to branch. As the preferential crystal growth direction was found to deviate by  $15^\circ$  from the heat flow direction, the system might have revealed conditions similar to growth of seaweed-like structures. However, whether these conditions caused the rapid advancement of dendrite-like object cannot be definitely clarified as convection rolls ahead of the array may also recurrently alter the solute boundary layer.

## Acknowledgements

This work was supported in part by the European Space Agency ESA through means of the ESA map project METCOMP and in part by the Austrian Space Agency ASA within the frame of the project METTRANS-ISS.

## References

- [1] T.W. Clyne, Heat flow in controlled directional solidification of metals, Part I, *J. Crystal Growth* 50 (1980) 684-690.
- [2] T.W. Clyne, Heat flow in controlled directional solidification of metals, Part II, *J. Crystal Growth* 50 (1980) 691-700.
- [3] J.J. Favier, Recent advances in Bridgman growth modeling and fluid flow, *J. Crystal Growth* 99 (1990) 18-29.
- [4] P. Busse, F. Meissen, Coupled growth of the peritectic  $\alpha$ - and the peritectic  $\gamma$ -phases in binary titanium aluminides, *Scripta Mater.* 36 (1997) 653-658.
- [5] S. Dobler, T.S. Lo, M. Plapp, A. Karma, W. Kurz, Peritectic coupled growth, *Acta Mater.* 52 (2004) 2795-2808.
- [6] W. Kurz, R. Trivedi, Banded solidification microstructures, *Metallurgical and Materials Transactions A*, 27 (1996) 625-634.
- [7] A. Ludwig, J.P. Mogeritsch, M. Grasser, In-situ observation of unsteady peritectic growth modes, *Transactions of the Indian Institute of Metals* 62 (2012) 433-436.
- [8] J.P. Mogeritsch, S. Eck, M. Grasser, A. Ludwig, In situ observation of solidification in an organic peritectic alloy system, *Materials Science Forum* 649 (2010) 159-164.
- [9] W. Kurz, D.J. Fischer, *Fundamentals of solidification*, Trans tech Publications Ltd 1998 [ISBN 0-87849-804-4].
- [10] M. Barrio, D.O. Lopez, J.L. Tamarit, P. Negrie, Y. Haget, Degree of miscibility between Non-isomorphous plastic phases: Binary System NPG-TRIS; *J. Mater. Chem.* 5 (1995) 431-439.
- [11] W.J. Boettinger, The structure of directionally solidified two-phases Sn-Cd peritectic alloys, *Metall. Trans.* 5 (1974) 2023-2031.
- [12] R. Trivedi, J.S. Park, Dynamics of microstructure formation in the two-phase region of peritectic systems, *J. Crystal Growth* 235 (2002) 572-588.
- [13] R. Trivedi and J.H. Shin, Modelling of microstructure evolution in peritectic systems, *Mater. Sci. Eng. A* 413-414 (2005) 288-295.
- [14] Information on [http:// www.merck.de](http://www.merck.de)
- [15] M. Barrio, D.O. Lopez, J.L. Tamarit, P. Negrier; Y. Haget, Molecular interactions and packing in molecular alloys between non-isomorphous plastic phases, *J. Solid State Chem.* 124 (1996) 29-38.
- [16] <http://en.wikipedia.org/wiki/Tris>
- [17] J.P. Mogeritsch, A. Ludwig, S. Eck, M. Grasser, B.J. McKay, Thermal stability of a binary non-faceted/non-faceted peritectic organic alloy at elevated temperatures, *Scripta Mat.* 60 (2009) 882-885.
- [18] Information on <http://www.sigmaaldrich.com>
- [19] Information on <http://www.vitrocom.com>
- [20] Y. Chen, B. Billia, D. Z. Li, H. Nguyen-Thi, N. M. Xiao, A. Bogno, Tip-splitting instability and transition to seaweed growth during alloy solidification in anisotropically preferred growth direction, *Acta Mat.* 66 (2014) 219-231.