

## ***In situ* observation of solidification in an organic peritectic alloy system**

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**Abstract.** Up to date very few organic substances have been reported that show a non-faceted/non-faceted (nf/nf) peritectic phase diagram in a temperature range suitable for direct observation in a micro Bridgman furnace setup. Sturz et al. [1] and Barrio et al. [2] studied the peritectic phase diagram for the organic model alloy TRIS (Tris(hydroxymethyl)aminomethane) - NPG (Neopentylglycol). The phase diagram is based on thermal analysis by means of DSC measurements [1, 2] and evaluation of lattice parameters measured with x-ray diffractometry [2]. In the current work we present investigations on the system TRIS – NPG that have been obtained by optical investigations of directional solidification in a micro Bridgman-furnace with various initial alloy concentrations and pulling rates in a fixed temperature gradient. The phase diagram [1, 2] was confirmed by direct comparison of DSC measurements and optical investigations. Furthermore we present in situ observations of solidification in the peritectic region. They show a solidification behavior that was clearly distinguishable from the solidification in hyper- and hypoperitectic regions of the phase diagram.

### **Introduction**

**Phase diagram.** Fig 1. presents the phase diagram of the organic model alloy TRIS -NPG which shows a nf/nf peritectic reaction as published by Barrio et al. [2]. Both substances show an orientationally disordered crystal (ODIC) phase, called “plastic phase” at high temperature. This fact permits the investigation of a nf/nf peritectic phase. In the current work investigations of the solidification morphology of the NPG-TRIS system are presented that have been obtained by optical investigations of directional solidification in a micro-Bridgman furnace with a fixed temperature gradient of  $1.4 \times 10^4$  K/m. Detailed descriptions of the setup and investigations on the stability of the used substances in the given set-up have been published recently [3].

**Peritectic solidification.** A peritectic reaction is in general the transformation of a liquid and an already existing solid primary phase  $\alpha$  to a second solid phase  $\beta$  ( $L + \alpha \rightarrow \beta$ ). Influenced by convection, temperature gradient, initial composition, cooling rate, and physical properties of the alloy, a wide variety of possible microstructures have been observed. Due to different diffusion mechanisms, solid-to-solid transformations are generally much slower than liquid to solid transformations. As a consequence, peritectic reactions are in many cases far away from a “thermodynamic equilibrium” situation. “Micro structure maps” plot the morphology as a function of alloy composition and the  $G/V$  ratio, where  $G$  is the temperature gradient in the sample and  $V$  the growth velocity [4, 5]. Thus, these maps indicate which solidification morphologies are expected for given concentration, temperature gradient, and growth velocity assuming steady-state growth conditions. According to literature [6, 7, 8, 9] the second phase  $\beta$  grows directly from interdendritic

liquid with high growth rates and, in many cases, both solid phases grow in parallel. Below the critical growth velocity  $V_c$  it is possible that both phases an oscillatory formation of the primary and the second phase occurs as described in [10].

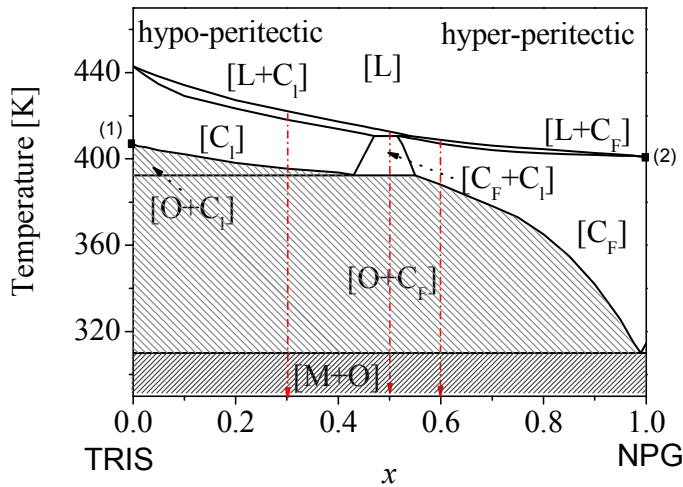


Figure 1. TRIS - NPG phase diagram modified after Barrio [2]. In the dark shaded region both substances  $[M + O]$  are faceted and not miscible. In the bright shaded region the faceted phase  $[O]$  and the plastic phase  $[C_F]$  or  $[C_I]$  coexist. The dotted lines show the positions of the concentration of the investigated alloys (fig. 3 – fig. 5). The black points are the solid/solid phase transition of pure TRIS and the melting point of pure NPG.

### Experimental Set-up

**The Bridgman furnace and imaging device.** For optical investigations a micro Bridgman-furnace as described in [3] was used. For all images shown in this work a glass capillary tube with an inner diameter of  $0.1 \times 20$  mm and a wall thickness of 0.1 mm was taken [11]. The microscope is equipped with a CCD camera which allows the measurement of positions in the field of view. Fig. 2 shows a typical image of a single 20 mm wide capillary sample. The sketch below the image illustrates how the temperature of the planar solid – liquid interface could be deduced from the position in the set-up and the known temperature field defined by the melting point of pure NPG (fig.1(1)) and the solid/solid transformation of pure TRIS (fig.1 (2)).

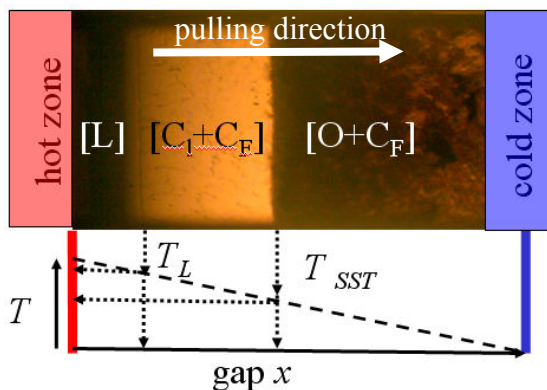


Figure 2: Picture of a single capillary sample in a temperature gradient field. The position of the planar solid/liquid ( $T_L$ ) and solid/solid transformation front can be clearly differentiated. The sketch below the image illustrates how the temperature of the solid/liquid interface was deduced from its position in the set-up based on a known temperature field.

**Chosen material and boundary conditions.** The organic substances used for this work - NPG and TRIS - were bought from the commercial supplier Aldrich [12] with an indicated purity of 99 % and 99.9+ %, respectively. NPG was dried and TRIS was used as delivered. Liquid TRIS and alloys of the organic substances show a concentration- and temperature-sensitive instability as reported in Mogeritsch et al. [3] which are limited by the boundary conditions for the temperature gradient  $G$  and the pulling rate of the glass tubs in the micro Bridgman- furnace.

### In-situ observation

First in-situ observations of capillaries filled with various alloy composition in a defined linear temperature gradient showed that all plastic phases occurred with almost the same opaque color. Only the solid/solid interface between the opaque plastic phases  $[C_I]$  and  $[C_F]$  and the dark faceted phase  $[O]$  is visible (fig. 2). To distinguish between the plastic phases  $[C_I]$  and  $[C_F]$ , concentrations in different regions are investigated (indicated as vertical lines in fig. 1) under the same boundary conditions. The fixed boundary conditions were  $0.9 \mu\text{m/s}$  for the sample pulling rate and  $1.4 \times 10^4 \text{ K/m}$  for the temperature gradient. The hypoperitectic and the hyperperitectic region show clearly two different solidification morphologies under the same conditions. The picture (fig. 3) shows the solidification morphology for the alloy with a concentration in a region where the plastic phase  $[C_I]$  occurred. Starting with a planar front at  $t = 0$  the solidification morphology changes soon to a dendritic one and stays dendritic.

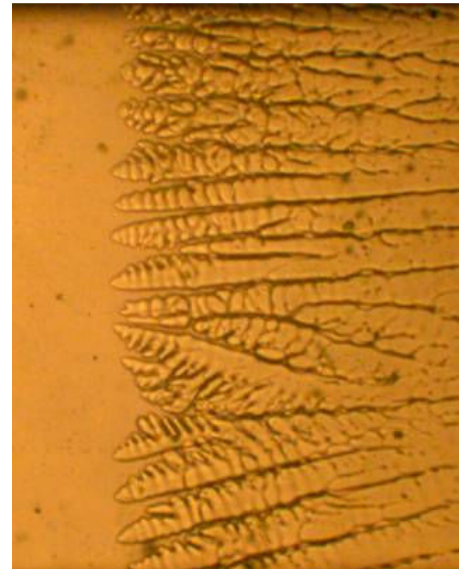
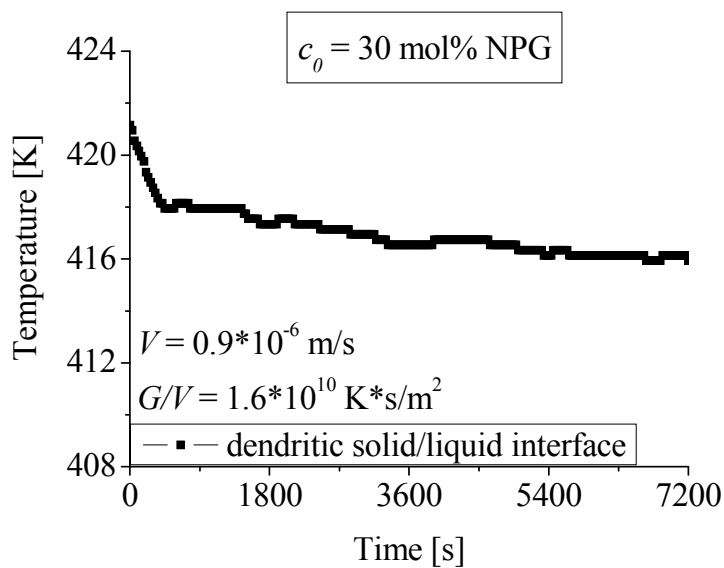


Figure 3: The graph on the left hand shows the temperature of the solid/liquid interface as a function of time. The interface shows clearly dendritic solidification morphology as displayed in the picture on the right hand side .

The solidification morphology of an alloy with a much significant higher NPG concentration in the hyperperitectic region occurs as a planar front (Fig. 4). Here the solid/liquid interface shows a stable planar front with a constant solidification temperature at 405 K after approximately 2700 s ( $\sim 45$  minutes). The graph on the left hand side in Fig. 4 relates the appearance of the solid/liquid interface according to the interface temperature and the observation time.

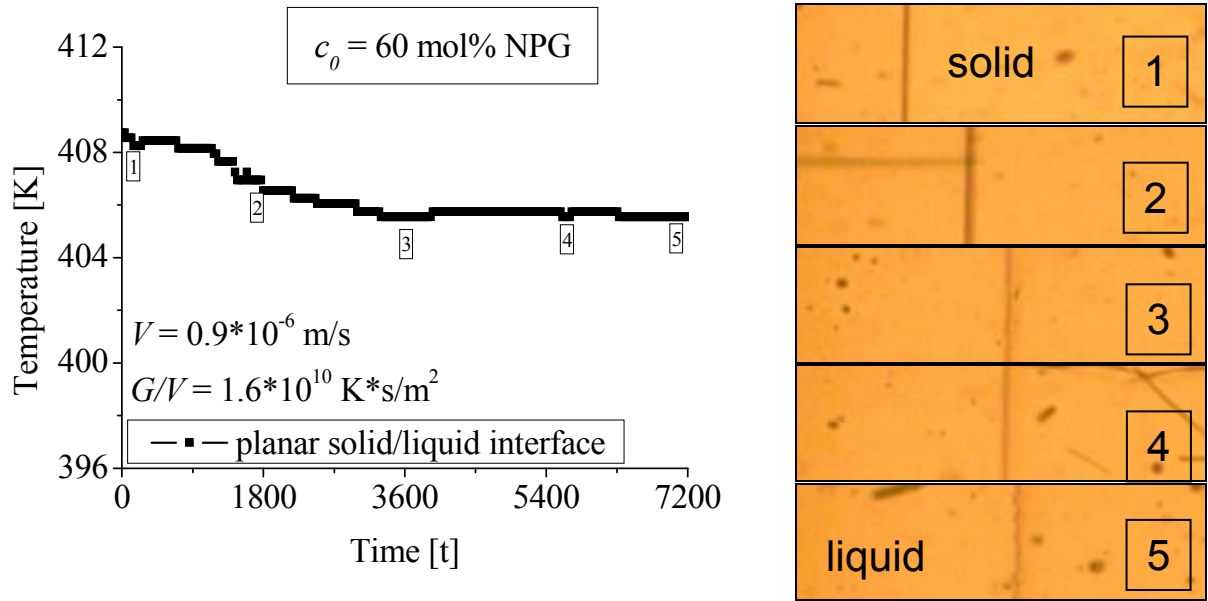


Figure 4. The morphology of an alloy with hyperperitectic solidification occurs as a planar solid/liquid interface. The pictures correspond to the numbered positions in the graph on the left hand side. It shows the temperature of the planar solid/liquid interface as a function of time.

In the hypoperitectic region within the peritectic plateau the solid/liquid interface, for alloys close to the peritectic point showed a strong oscillation (see Fig. 5). Furthermore, a change in the morphology occurs. The morphology changes from dendritic to cellular/planar solidification and back.

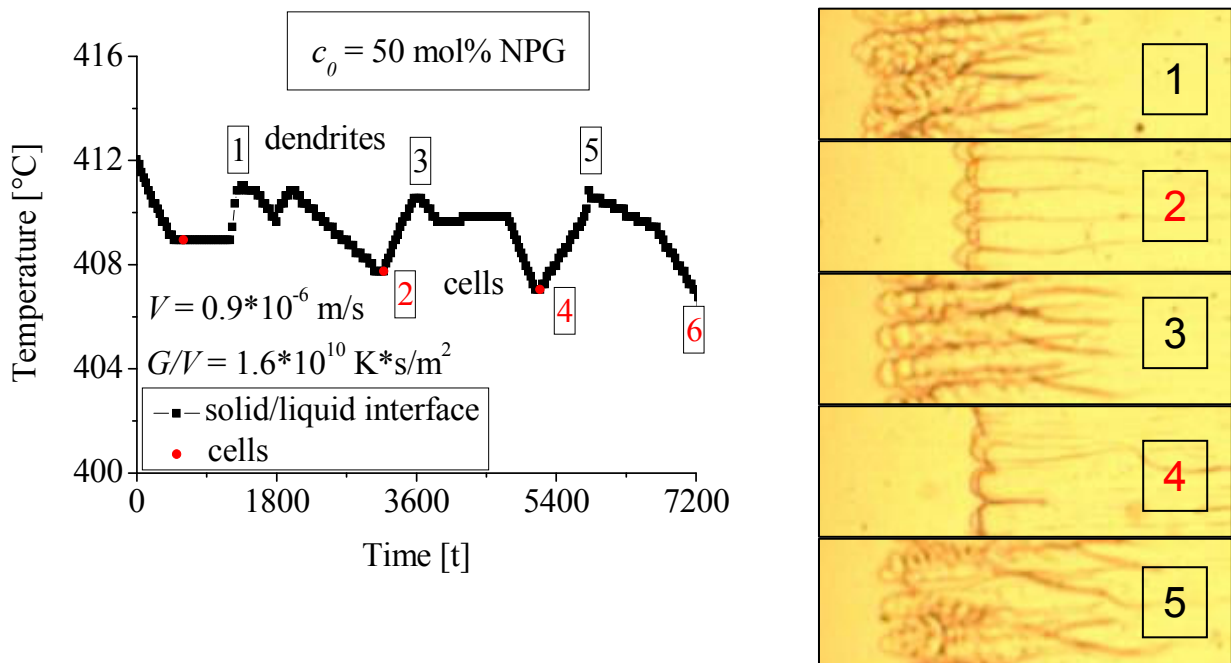


Figure 5: The graph on the left hand side shows the temperature of the solid/liquid interface as a function of time. The interface shows oscillation of the solid/liquid interface. The pictures on the right hand side reflect this fact as indicated in the graph. The cellular/planar interface regions are marked with red dots and red numbers.

In fig. 6a and 6b the oscillation of the solidification morphology is displayed in more details. One oscillation time period requires approximately  $2109 \text{ s} \pm 169 \text{ s}$  when the alloys solidified over a length of  $1.89 \text{ mm} \pm 0.15 \text{ mm}$ . The time period and the width of one period remain in this experiment constant. However, the time to grow increase dendritic increase from period to period.

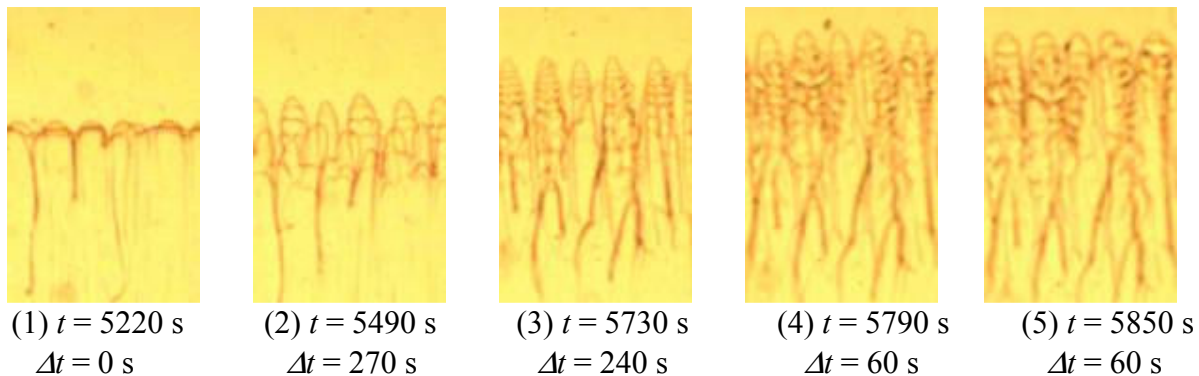


Figure 6a: Details of one oscillation period from point 4 to 5 (Fig. 5).  $t$  shows the absolute time position in Fig. 5 and  $\Delta t$  the time difference to the next picture.

Fig. 6a shows the solid/liquid interface with a higher growth rate as the pulling rate. Here the solid/liquid interface changes its morphology from a cellular/planar front (1) to dendrites (2). The dendrites grow against the pulling rate until the interdendritic liquid starts to solidify (4). As soon as the dendrite tips reach the maximum temperature (5) the tip radius increase.

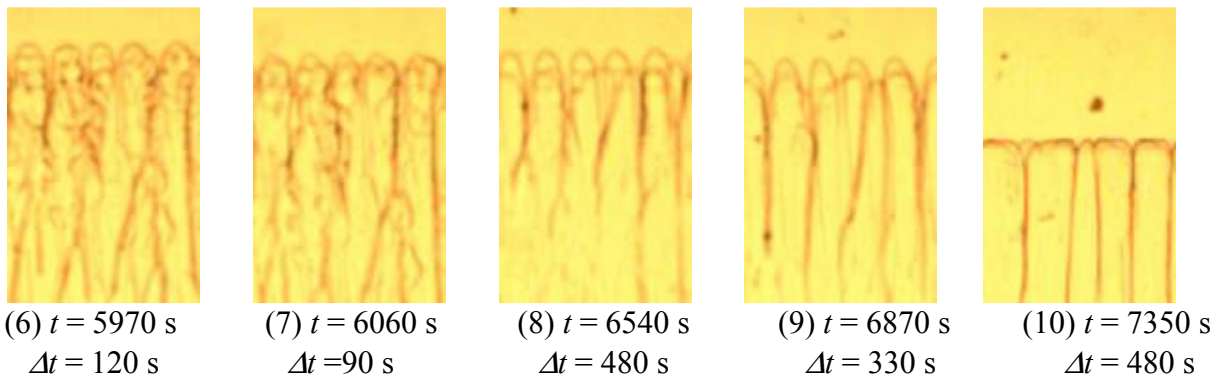


Figure 6b: Details of one oscillation period from point 5 to 6 (Fig. 5).  $t$  shows the absolute time position in Fig. 5 and  $\Delta t$  shows the time difference to the next picture.

Fig. 6b shows the change of the solid/liquid morphology with a lower growth rate as the pulling rate. At the highest solid/liquid interface temperature the morphology changes from dendrites (6) to a cellular/planar front (10). At first the region of the interdendritic liquid increases from picture (7) to (8) and afterwards the dendrites transform to cells (9) and to a cellular/planar front (10). It has to be mentioned that the effective diffusion coefficient  $D_{eff}$  of the binary phase diagram is not known and subject of further investigations. Therefore, it was not possible up to know to calculate a micro structure map which describes the expected solidification morphology, as mentioned [4]. But preliminary investigations show that the oscillation occurs at a  $G/V$  ratio where both phases solidify not planar (above the limit of constitutional undercooling). In this region (pulling rate of  $0.5 \mu\text{m/s}$  to  $0.9 \mu\text{m/s}$ ) the primary phase solidifies as dendrites where the secondary phase forms cells or stays planar (see fig. 4, point 5). Additionally, the oscillating solidification was not formed under steady-state conditions and did not accomplish the assumptions for layered structure formation formulated in [10]. During solidification one phase follows the solidus line before the secondary phase starts to nucleate on the solid/liquid interface. At this state the undercooling is sufficient that the secondary phase form dendrites. From this time on it is not possible to differ between the phases, but it seems

that always both phases are present and solidify in a competitive manner. Further investigations are necessary to understand the oscillating solidification in more details.

### Conclusions:

Based the presented observations the following is stated:

- Solidification morphology of hypoperitectic alloys show dendritic micro structure. The results could be reproduced by several experiments but a stable planar front was not found.
- Optical investigations in the hyperperitectic region showed a stable planar front for NPG rich alloys.
- For hypoperitectic alloys with concentrations at the peritectic plateau strong oscillation were observed. Especially for alloys around the peritectic plateau, further investigations will be performed in future.

Since the optical observation is based on just one pulling velocity further studies are required with varying pulling speeds. In addition it has to be kept in mind that convection can play an important rule as reported in [10, 13].

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