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In-situ observation of the dynamic of peritectic coupled growth using the binary organic system TRIS-NPG

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Abstract. This paper shows the evolution from banded structure to peritectic coupled growth and describes the mechanism which leads to such microstructure formation. Experimental investigations on binary organic TRIS-NPG (Trishydroxymethyl-aminomethane, Neopentylglycol) alloys at concentrations in the peritectic region were carried out in order to study the formation of peritectic microstructures. The experiments were done vertically with relatively large rectangle glass tubes so that slow natural convection occurred. Each time a sample was hold unmoved in the vertical micro Bridgman-furnace for 2 hour to establish a constant temperature gradient. Afterwards, the samples were moved at several pulling rates through the furnace and a camera recorded the dynamic of the solid/liquid interface. The in-situ observations show layered structures for concentrations within the hyper-peritectic region. Carefully evaluations of the results exhibit, that (i) the solid/liquid interface is curved in observation direction toward the glass walls, (ii) the initial existing peritectic phase grows at micrometer-sized liquid channels inside the primary phase toward to the solid/liquid/glass wall junction, (iii) afterwards the peritectic phase spreads along the liquid-primary phase boundary and forms a so-called band, then (iv) the primary phase gets largely overgrown and unstable peritectic coupled growth (PCG) forms; (v) this PCG is inherent unstable and disappears and occurs in several cycles; until (vi) finally stable growth of the primary phase prevails.

1. Introduction

The interesting characteristic in peritectic systems is the possibility of forming peritectic phase β above the peritectic temperature T_p . In direct solidification experiments with a large temperature gradient/solidification rate (G_T/V) ratio the microstructure is governed by solute transport and nucleation kinetic. This can enable layered microstructure patterns like bands, islands or peritectic coupled grow (PCG). Trivedi [1] published a theoretical model under purely diffusive condition to explain banded microstructures. The model predicts bands in the two phase region $c_{p\alpha} < c_0 < c_{p\beta}$ (hypo-peritectic composition) with an oscillating solid/liquid interface above and below the peritectic temperature T_p . Karma et al. [2] introduce a quantitative model of banding in purely diffusive and strongly convective regimes which explains experimentally observed bands within the two phase region $c_{p\beta} < c_0 < c_L$ (hyper-peritectic composition). Mazumder et al. [3] investigated Sn-Cd and Pb-Bi alloys and observed a new morphology of island bandings consisting of the peritectic phase inside the continuous matrix of the primary phase. They developed a physical mechanism for microstructure formation which is supported by a numerical model. In contrast to the banded structure Lee et al. [4] found eutectic-like two-phase microstructures in Ni-Al alloy. Trivedi and Park [5] did experimental investigations with Sn-Cd alloys to evaluate the role of nucleation on periodic microstructure formation. They found out that



under diffusive growth conditions the microstructure depends on the growth competition of the nucleated phase and the existing phase. In extra thin samples only a single nucleus of the new phase forms which grows laterally. In large samples multiple nuclei can occur. Thus, the nucleation distance and the competition between the lateral and parallel growth of both phases determines the microstructure pattern [5]. Lo et al. [6] carried out corresponding experiments in combination with phase field simulations. They found that island banding disappears or acts as a transient microstructure which leads to coupled growth. Whereby, two preconditions must be satisfied: (i) a stable range of coupled growth spacing must exist; and (ii) the mean distance between islands must fall approximately within this stable range. Otherwise the lamellae will be erased.

To deepen our understanding of layered structures we performed investigations of the solid/liquid interface dynamics and the occurring microstructure formations by using transparent organic model substances. Experiments were carried out in extra thin rectangle glass samples (inner dimensions $2.0 \times 0.1 \text{ mm}^2$) in order to suppress convection and relatively large rectangle glass samples (inner dimensions $6.0 \times 0.6 \text{ mm}^2$) which enables slow natural convection, with pulling velocities close to the stability limit of both solid phases. The experimental results for the extra thin samples show bands, islands and isothermal peritectic coupled growth in the hypo-peritectic region and are published in [7-12]. Large rectangle samples exhibit layered structures in the hyper-peritectic region. The observed layered structures exhibit initial band formations which leads to PCG. Ludwig et al. [13] published the results for $c_0 = 0.52$ mol fraction NPG, at $V = 0.13 \text{ } \mu\text{m/s}$ and in the present paper, we report in-situ observations from banded structures to isothermal PCG for $c_0 = 0.53$ mol fraction NPG, at $V = 0.16 \text{ } \mu\text{m/s}$.

2. Experimental Set-up

The solidification experiments were done with an alloy consisting of the organic components TRIS (Trishydroxymethyl-aminomethane) and NPG (Neopentylglycol) [14-16]. Both components [17, 18] show high temperature non-faceted phases which solidify in a planar, cellular or dendritic manner like metals. The peritectic region goes from $c_{p\alpha} = 0.47$ to $c_L = 0.54$ mol fraction NPG with the peritectic concentration at $c_{p\beta} = 0.51$ mol fraction. Detail information of the TRIS-NPG phase diagram are given in [17, 19]. Investigations were carried out in steps of 0.1 mol fraction NPG over the whole peritectic region.

For the experiment, filled large rectangle glass sample (inner dimensions $6.0 \times 0.6 \text{ mm}^2$) was placed into the preheated micro Bridgman furnace [19] and held at least 120 minutes to establish a thermal equilibrium and a planar solid/liquid interface. Afterwards, the sample was pulled with a constant pulling rate through the furnace for at least 9 hours. The experimental investigations were done with a constant temperature gradient of $G_T = 6.6 \text{ K/mm}$ and pulling velocities that ranges from $V = 0.09 \text{ } \mu\text{m/s}$ to $1.9 \text{ } \mu\text{m/s}$ for each selected concentration. Different formations of bands, island bands and peritectic coupled growth were found for all concentrations within the hyper-peritectic region (0.52 - 0.54 mol fraction). In this paper only the experimental result of an alloy with 0.53 mol fraction NPG is presented.

The micro Bridgman-furnace was made up of two brass parts fixed on symmetrical ceramic shelters to create a 7 mm adiabatic gap, see Fig. 1. The temperature within the brass parts was controlled by electrical resistant heaters and measured with Pt 100 temperature sensors placed inside each brass block. A slot ($6.5 \times 1.2 \text{ mm}^2$) was milled into the brass blocks to fix the glass sample. The sample was illuminated through glass windows in the ceramic plates at the adiabatic zone in order to observe the morphology of the solid/liquid interface with a ZEISS microscope in combination with a camera. In this paper we define the glass wall next to the illumination as the backward side and the glass wall close to the camera as the front side. During solidification images were recorded with $\Delta t = 30 \text{ s}$ simultaneously with relevant temperatures. The movement of the glass sample through the furnace was PC-controlled. Details on alloy preparation, filling and sealing of the sample, as well as on the Bridgman-furnace can be found at [6-12, 19].

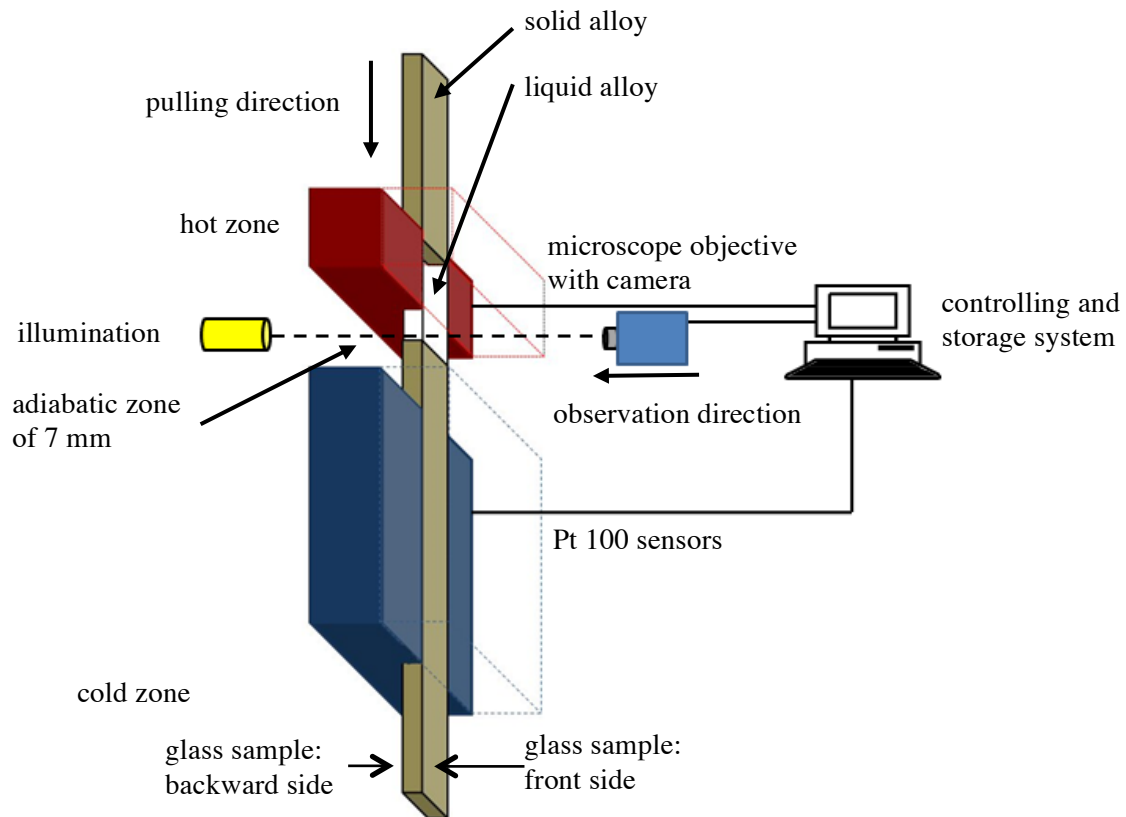


Figure 1: Sketch of the micro Bridgman-furnace. The brass parts of the front ceramic shelter (not shown in the sketch) and the solid alloy within the glass sample are full colored. The brass parts on the front ceramic shelter and the liquid alloy are shown transparent. The glass sample has inner dimensions of $6.0 \times 0.6 \text{ mm}^2$ and a wall thickness of 0.4 mm .

3. Results

The initial microstructure exhibits a polycrystalline solid/liquid (s/l) interface. Below this first interface, the polycrystalline grains of α phase are surrounded by liquid until further down a second interface is visible, the transition from the $\alpha-l$ region to the $\beta-l$ region. The final microstructure formation after approximately 9 h is shown in Fig. 2 and illustrates the following different pattern from bottom to top:

- The initial polycrystalline form of the grains is still visible below the initial second interface.
- Above the initial second interface there are some small NPG enriched liquid inclusions (droplets), which are leftover initially surrounding the α phase.
- Formation of one layered structure in form of a β phase band.
- Unstable heart-like shaped β phase surrounded by α , formed by unstable PCG.
- Change into another tulip-like unstable PCG which reveal a much finer spacing.
- Disappearing of α lamellae and formation of a second β island band.
- Another cycle of unstable PCG starting again with relative large α regions. Quickly the thickness of the α lamellae decreased and those of β increases.
- This time PCG disappears by first an increase and then an abrupt disappearing of β , whereby now no β band forms but multiple β lamellae “survive” and start to form newly PCG. During these two last cycles, the β lamellae have again kind of tulip-like shape and instabilities which resemble $2-\lambda$ oscillations.

- PCG structures finished abruptly, except for few isolated PCG (left side of Fig. 2) which disappear after three additional cycles.
- The s/l interface slightly curved normal to the observation direction, but strongly in observation direction. This becomes obvious by grey diffuse line below the sharp s/l interface. The grey line accompanies the sharp s/l interface since the formation of the β band. As discussed in a former publication of the authors [11] curving of the interface can be understood by segregation originated by the thermo-solutal convection within the sample.

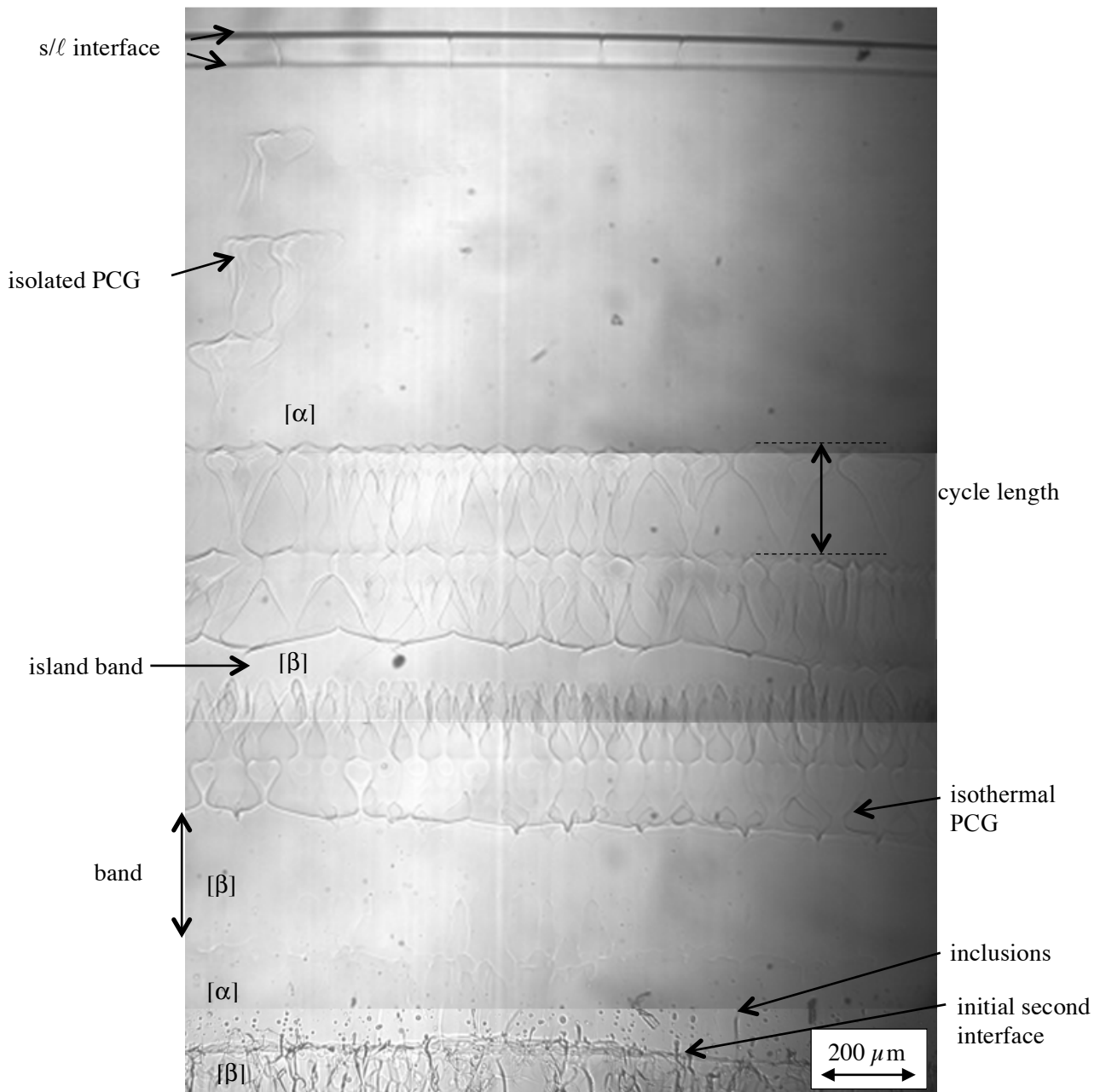


Figure 2: Microstructure formation of the organic compound TRIS-NPG at pulling rates close to the constitutional undercooling. Note that the shadowy black points were objects located outside of the sample. The figure is a compilation of three pictures taken at around 5, 7 and 9 hours after start pulling.

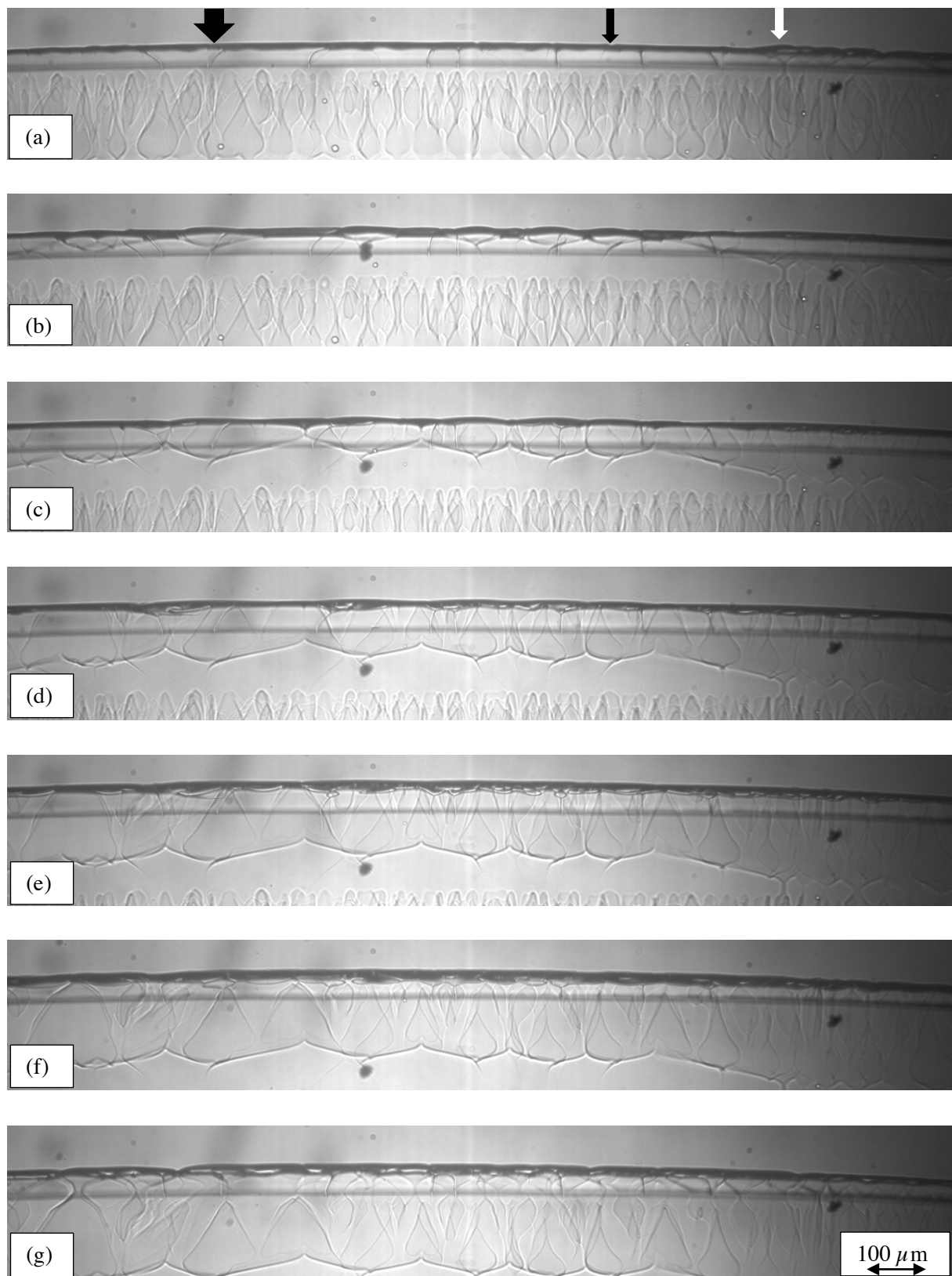


Figure 3: Details of one oscillation cycle. The sequence shows the dynamic of the s/l interface with a time step of 540 s.

4. Discussion

Both solid phases are transparent and the contrast is only given by phase boundaries, impurities and inclusions. After the sample is thermally equilibrated for 120 minutes the alloy is totally molten and transparent above the polycrystalline s/ℓ interface. Below this temperature, the solid phases α and β consist of polycrystalline grains (not shown). Below the s/ℓ interface the crystals of α phase are surrounded by liquid until further down a second interface indicates the transient from α to β phase. The huge amount of grains and inclusions occur mostly blurred and diffuse. In microscopy, the depth of field is very short, here only $55\ \mu\text{m}$, compared to the illumination through a $600\ \mu\text{m}$ thick layer of organic compounds. As a consequence, sharp grain boundaries can only be obtained by focusing on the front section of the solid alloy, approximately $100\ \mu\text{m}$ after the front glass wall.

With the beginning of pulling the α -phase starts to grow. Since the growth rate is smaller than the pulling rate the interface recoils, namely from liquidus towards solidus. Simultaneously, the second interface moved with the sample almost the whole withdrawal distance. Delayed in time, the β -phase grows then from the moving second interface along liquid channels though the α - ℓ region up to the initial position of the second interface. At that time, β spreads perpendicularly to the sample axis and forms a β -band. At this stage in time, the α and β phases are more or less polycrystalline but the liquid surrounding the grains has either vanished or transferred to liquid channels, or to round or elongated liquid inclusions (droplets).

The growth of the β band goes hand in hand with the appearing of a diffusive gray line. We assume that this blurry line is the glass wall s/ℓ interface junction. Please note, the diffusive gray line occurs below the polycrystalline s/ℓ interface. As we have never achieved to well focus the diffusive line, we believe that the s/ℓ interface reveals some curvature when approaching the glass wall. From studies with extra thin rectangle glass samples, the strong curvature of the s/ℓ interface close to the glass wall is well known. Also it is conceivable that the contact line between the rear glass wall and the s/ℓ interface has a similar appearance. However, we were not able to clearly observe the rear contact line. Indeed, sometimes we have the impression that the blurry line might be representing two overlaying blurry lines rather than one.

Careful observation of the dynamics of the interface exhibits that from the afore mentioned blurry line, a well-focused sharp line travels towards the s/ℓ interface in the bulk of the sample. This observation suggests that β growth from the band at the glass wall towards the sample center. Shortly before the β phase envelops completely the remaining α phase, PCG occur. The first cycle exhibits heart-like shaped β lamellae structures, Fig. 2. The next cycle exhibit that the lamellar spacings increase first slightly and later form tulip-like shaped formations. Subsequently, the amount of lamellae increases approximately 2 to 3 times and overlaps in such a way that a β island band occurs.

Although the β phase overgrows nearly the α phase a new cycle of PCG occurs. The lamellae spacing of the new cycle in nature is non-uniform and shows a transition from heart-like shape growth to tulip-like or even $2\text{-}\lambda$ oscillation growth, see cycle three in Fig. 2. All β lamellae spacing in common is the increasing of the horizontal growth velocity shortly before the lamellae is nearly erased. Afterwards, a last fourth cycle of PCG with $2\text{-}\lambda$ oscillation lamellae spacing and heart-like shaped comes into being. The layered solidification structure finished abrupt, except for 3 additionally isolated layered structures cycles. The final solidification pattern shows a planar α phase s/ℓ interface.

The dynamics of the s/ℓ interface during the formation of the third PCG cycle is shown in more details in Fig. 3a-g. The picture sequence covers the time period from 11,160 s to 14,400 s with a time step of 540 s. All pictures reveal a slightly curved dark s/ℓ interface followed by a grey blurry line some $40\ \mu\text{m}$ behind. The grey blurry line is the result of the curvature of the s/ℓ interface in observation direction as mentioned above. The dark dot at the right side is an impurity outside the glass sample.

The sequence starts with the growing of the β island band. Beginning from the left side toward the center the first picture (Fig. 3a) illustrates the following important features: (i) fine curved lines which follow the s/ℓ interface curvature. One of it is indicated with a thick black arrow. We interpret these fine lines as grain boundaries separating grains of the same solid phase. It is quite important to notice, that during the course of a cycle these fine lines continue to exist. (ii) It is also observable that the grain boundaries are the origin of the appearance of patches of the other solid phase. Such a position is indicated with a small black arrow. (iii) The far right side of the pictures shows an already wavy s/ℓ interface. Beginning with small patches a new solid phase starts to grow, marked with a white arrow. As can be seen in Fig. 3b-c those patches appear from the s/ℓ interface and successively spread over the whole interface. The blurry character of the phase boundary assumes that the patches are growing close to the center of the sample. We recognize this new phase in Fig. 3 a-b as α phase.

Fig. 3c-d shows that the growing α phase spreads perpendicular to the sample axis and toward the observation direction in such a way that they form nearly a new band. Additionally, PCG is visible within the α phase patches which are supposed to be located some distances away from the growing α phase, probably in the center of the sample. Then having spread nearly over the whole interface the α phase goes through the focus which means that the phase is now close to the front wall. At the same time, the β lamellae spacing of the PCG beyond the α phase increase and new patches at the s/ℓ interface becomes visible, Fig. 3d. From the interpretation of the PCG, it can be concluded that the β phase grows perpendicular and in observation direction. PCG exhibits a tulip-like shape but considering the three dimensionality of the sample a cone-like shape is more precise. In Fig. 3d-f the β phase reach down to the front side and the phase boundaries are within the focus. We understand this circumstance that the β phase is between the center and the front side of the sample.

In Fig. 3g the growth of a new phase is observable. The s/ℓ interface gets wavy and new patches are visible. We interpret this as the growing of the α phase similar to the beginning of the cycle, Fig. 3a.

5. Conclusions

Experimental results in binary organic TRIS-NPG alloy have been presented that exhibit complex microstructure formation in the presence of convection. The main finding of the present work is the in-situ observation of cycles of band formation and unsteady peritectic coupled growth. Note that the evaluation of the interface dynamic with the recorded video is much easier than presenting a sequence of pictures. However, careful observation of the dynamics of the s/ℓ interface shows the transformation from banded structure to an unsteady peritectic coupled growth. In the presence of convection the s/ℓ interface becomes curved toward the sample wall. The corresponding concentration profile ahead of the solidification front enables the growth of the peritectic phase close to the sample wall which leads to a α phase matrix covered by a β phase (probably both in the foreground and in the background). This circumstance leads to a competitive growth in parallel and lateral solidification direction. This is visible in form of heart-like shaped and tulips-like shaped β phase lamellae. Beginning with small patches, equal to the tip of the cone, the β phase spreads out in lateral and parallel direction. The increasing volume fraction of the β phase leads to a single island. As soon as the α phase is preferred the tulip-like cones are quickly reduced to small patches and the solidification pattern starts again with an increasing volume fraction of the β phase. This cycle is visible by instabilities between the patch and the maximum size of the cone. The solidification mechanism shows a relatively large volume fraction of β but the phase cannot fully cover the α phase. Finally, the α phase grows stable in form of a planar s/ℓ interface.

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