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In-situ observation of coupled peritectic growth in a binary organic model alloy

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ABSTRACT

Peritectic alloys form a variety of solidification morphologies of which peritectic coupled growth (PCG) is the most peculiar. Because the conditions that lead to PCG are still under discussion, in-situ investigations of the evolution from lateral bands to PCG were carried out by using binary organic TRIS-NPG model alloys at concentrations in the peritectic region. The experiments were done vertically with relatively large rectangle glass tubings. For a hyper-peritectic alloy at growth rates below the morphological stability limits of both solid phases, we found that first the properitectic phase grew while lateral bands of the peritectic phase formed between the glass walls and the properitectic phase. Then, the peritectic phase dominated the growth until lateral bands of the now properitectic phase occurred, again close to the glass walls. Now both phases grew side-by-side as two layers at different depths in the sample. However, the properitectic phase spread locally onto the peritectic/liquid interface, so that patches of peritectic phase surrounded by a properitectic matrix developed. This resulted in creating an unstable PCG mode with cycles of increasing and decreasing phase amounts, which from a side-on view resemble tulip- and onion-like structures respectively.

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1. Introduction

Many alloys of great industrial significance show a phase diagram with a peritectic reaction (steel, Al- and Cu-alloys, high T_c superconductors and rare earth permanent magnets) [1]. According to such phase diagrams, peritectic alloys form a primary α -phase first upon cooling from the melt and then at the peritectic temperature, T_p , a second solid β -phase called peritectic phase. Above T_p , the α -liquid equilibrium is stable and the β -liquid equilibrium is metastable, whereas the opposite is true below T_p . At T_p , a melt with concentration, c_p , is in equilibrium with the primary α -phase at $c_{p\alpha}$ and the peritectic β -phase at the so-called peritectic concentration $c_{p\beta}$. Alloys with $c_{p\alpha} < c_0 < c_{p\beta}$ are called hypo-peritectic and those with $c_{p\beta} < c_0 < c_p$ are called hyper-peritectic. Here, c_0 is the initial alloy concentration.

For conditions where both phases are supposed to grow with a morphologically stable planar solid/liquid interface (s/ℓ interface), the transient growth process necessary to reach a steady-state growth with a planar s/ℓ interface of one phase is hindered by

* Corresponding author. E-mail address: johann.mogeritsch@unileoben.ac.at (J.P. Mogeritsch). the nucleation and growth of the other phase. This in turn then passes through a transient growth process, hindered by the nucleation and growth of the initial phase. This interplay between solute transport and nucleation kinetics leads to the formation of a banded structure consisting of layers of the two solid phases extended perpendicular to the growth direction [2–6].

A conceptual description of cyclic nucleation and growth under purely diffusive condition was suggested by Trivedi in Ref. [7]. However, Trivedi's ideal concept fails in many real solidification cases for three reasons. First, often the presence of melt convection changes the melt concentration locally as well as at the sample scale [8,9]. Second, the lateral spread of the phase which has just nucleated, competes with the forward growth of the present phase and thus incomplete bands - so-called islands or island banding form [10–12]. Finally, in real systems, the three dimensionality of an unsteady s/l interface motion may lead to a dynamic phase interaction where nucleation is of less importance [9]. In bulk samples the dominant growth of one phase can be accompanied by a simultaneous growth of a small amounts of the second phase somewhere in the sample. A sudden intensified appearance of the second phase might then look like nucleation but is in fact a rapid spread over the first phase.

In addition, lamellar- or rod-like peritectic coupled growth

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(PCG), similar to those typically observed in eutectics were found and presented in Refs. [9,13–16]. PCG reportedly only occurs when both primary and peritectic solid phases are morphological stable (cf. reference). Obviously, both PCG and island banding morphologies can form under apparently similar conditions. To investigate the underlying microstructure selection, Lo et al. [9] conducted both corresponding experiments and phase field simulations. They found that island banding may be either sustained in time, or in a transient microstructure that 'seeds' coupled growth. If that is the case, two basic conditions must be satisfied: (i) there must exist a stable range of coupled growth spacing; and (ii) the mean distance between islands must fall approximately within this stable range.

In the present paper, we report in-situ observations of the transition from banding to PCG using thick samples (3D) of an organic model system, which reveals a non-faceted/non-faceted two-phase peritectic alloy. The paper is structured by describing the experimental procedure in Section 2 and the corresponding insitu observations of banding and PCG in Section 3. For a correct identification of the different solid phases growing in the thick samples, we discuss in Section 4 features of the three-dimensionality of the observation, the formation of lateral bands, the transition between cycles of PCG, and finally, how isothermal PCG develops from banding. Conclusions and a summary are given in Section 5.

2. Experimental

The solidification experiments were carried out with alloys consisting of two organic components, namely TRIS¹ (Tris(hydroxymethyl)-aminomethane) and NPG (Neopentylglycol).² Both components show the presence of transparent high temperature non-faceted phases [17] (also called plastic phases), which are supposed to solidify with similar solidification morphologies as metals. The phase diagram shows a peritectic region from $c_{p\alpha} = 0.47$ to $c_p = 0.54$ mol fraction NPG with the peritectic concentration at $c_{p\beta} = 0.51$ mol fraction. Detailed information on the TRIS-NPG phase diagram as well as on important materials properties of NPG and TRIS can be found in Ref. [18]. Directional solidification experiments were carried out with alloy compositions in steps of 0.1 mol fraction NPG over the whole peritectic range. In this paper we present detailed studies with alloys that had of $c_0 = 0.52$ mol fraction NPG.

For the investigations, 200 mm long rectangular tubes with a width of 6.8 mm and a depth of 1.4 mm were used. The wall thickness was 0.4 mm so that the inner width and depth of tubes were 6.0 mm and 0.6 mm, respectively. The organic alloys inside the tubes were solidified vertically upwards with a constant pulling rate, V_{pull} , in a given temperature gradient, G. The reason for choosing these relatively thick tubes was the fact that post-mortem studies of cylindrical metallic alloy samples showed some threedimensional features of the formation mechanisms that results in PCG [9,14,16]. These experiments were also performed with a vertical upwards growth direction. The tubes were filled by capillarity under Argon atmosphere of about 80% (around 20 mm at the upper end was left empty) and then hermetically sealed with a glue [18]. Such samples were then placed into the preheated micro Bridgman-furnace and held at least 120 min in rest to establish a thermally equilibrated state and a planar s/ℓ interface. As a sample is longer than the heated zone, only a sample segment of around 10 mm in length was molten. The pressure increase, which may

originate from the expansion on heating and melting, was released by a solid material column at room temperature not filling 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; visible gaps and cracks occur as the faceted phase contracts on cooling. Hence, the heated and finally molten segment can easily push the solid segments aside, both at the top and bottom, and a pressure-free molten segment can form. Note that the results presented in this paper were gained by using newly filled samples in which the concentration can be assumed to be uniform along the sample's length. After the preheating period of 120 min, the sample was moved at constant velocity into the cold part of the Bridgman furnace and a digital camera recorded and stored pictures of the s/ \Re interface with a time interval of $\Delta t = 30$ s.

The micro Bridgman-furnace was made up of two brass parts fixed on symmetrical ceramic shelters to create a 7 mm adiabatic gap (Fig. 1). 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 slot $(6.5 \times 1.2 \text{ mm}^2)$ was milled into the brass blocks in which the glass sample could slide. The sample was illuminated through glass windows in the ceramic plates at the adiabatic zone to observe the morphology of the s/ ℓ interface with a ZEISS microscope, in combination with a black-and-white camera. During solidification, images were recorded simultaneously with the relevant temperatures of both brass parts. 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 in Refs. [18–23].

In order to describe the experimental findings in the next section a coordinate system is defined in Fig. 1. The longitudinal direction is taken as z-direction, the wide side of the rectangular tube (width) is taken as x-direction and the small side (depth) as ydirection.

Both non-facetted high temperature solid phases of the TRIS-NPG system, namely the TRIS-rich properitectic α -phase and the peritectic β -phase, are equally transparent and thus optically indistinguishable. The identification of the solid phases is therefore only possible by careful observation of their growth dynamics. This will be done in the discussion section. In the result section 3, we only name the two solid phases as first and second leaving the exact



Fig. 1. Sketch of the micro Bridgman-furnace. The brass parts of the backward 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.

¹ http://en.wikipedia.org/wiki/Tris.

² http://www.sigmaaldrich.com or http://www.merck.de.

identity undefined. However, in Section 4 it will be shown that the first phase is indeed the α -phase and the second phase the β -phase.

3. Results

As mentioned above, we have investigated numerous alloy concentrations covering the whole peritectic range using a temperature gradient of G = 6.65 K/mm and pulling velocities that range from $V = 0.09 \ \mu$ m/s to 1.9 μ m/s. PCG was found for hyperperitectic samples with $c_{p\beta} < c_0 < c_p$ with pulling velocities below the stability limit of both solid phases [20,21,24]. The results presented here were taken for $c_0 = 0.52$ mol fraction NPG, with $V = 0.128 \ \mu$ m/s. Fig. 2 shows a compilation of three pictures taken at around 5, 7 and 9 h after starting to pull. Note that the shadowy black points are objects located outside of the sample.

The microstructure shown in Fig. 2 illustrates the following important features:

- The s/ℓ interface reveals isothermal coupled growth of two different solid phases. Although both solid phases are transparent it is obvious that the s/ℓ interface is formed by alternating lamellae of α- and β-phases aligned in growth direction.
- The s/l interface is straight in x-direction (perpendicular to the observation direction), but curved in y-direction (along the observation direction). This becomes obvious by the grey diffuse line below the sharp s/l interface. A detailed discussion of this statement is given in Section 4.3.
- The isothermal peritectic growth is cyclic in nature with a characteristic cycle length and an alternative sequence of (i) a quite low volume fraction of the second phase; (ii) an increasing volume fraction of the second phase; (iii) a splitting of the second phase lamellae basically in two parts with primary phase



Fig. 2. Microstructure formation of a hyper-peritectic peritectic TRIS-NPG alloy at pulling rates below the stability limit of both phases. The figure is compiled of three pictures taken at different instants during the solidification sequence.

in between; and (iv) an abrupt disappearing of the second phase lamellae.

- The amount of second phase lamellae increase with time. During the course of five cycles the number of second phase lamellae doubles. During the first cycle no lamellae oscillations can be seen, whereas during the fifth cycle the lamellae shows a wavy appearance where the wavelength of oscillation is approximately equal to two times the lamellae spacing. This is called $2-\lambda$ oscillation in literature [25].
- Isothermal PCG starts from (island) bands of the two phases.

4. Discussion

4.1. Three dimensionality of the observation

As shown in Fig. 1, observations were made in transmission through a 600 μ m thick layer of organic compound. A contrast is only given by phase boundaries. Both solid phases are equally transparent and cannot be distinguished optically. In convention, we may term objects close to the microscopic lens as being in front and those close to the illumination as being in the background.

In order to discuss the optical features arising from the three dimensionality of the sample, Fig. 3 shows the microstructure at the end of the thermal equilibration and after moving the sample under constant conditions for two different instants of time. After the sample is thermally equilibrated for 120 min the alloy is molten on the hot side and polycrystalline on the cold side. The liquid part is totally transparent, whereas the polycrystalline part is full of grain boundaries and thus full of blurred and indistinct lines (Fig. 3a). Sharp grain boundaries can only be seen by focusing on the front part of the polycrystalline microstructure. They are of course overlaid by blurred grain boundaries from the background. We usually focused throughout the experiments on the front part of the sample. Therefore, pictures like Fig. 2 show sharp phase boundaries located closer to the front inner glass wall. Unsharp phase boundaries are located more in the rear of the sample. Another important feature which helps to evaluate the location of specific phase boundaries is the presence of liquid inclusions. After thermal equilibration, the polycrystalline region is separated from the fully liquid region by a planar interface approximately at the liquidus temperature (Fig. 3a). Just below this interface the polycrystals are surrounded by liquid until further down a second interface is visible. According to the phase diagram this second interface marks the transient from the two phase α -liquid region to the two phase β -liquid region at T_p .

When we began to move the sample, the α -phase started to grow into the liquid while solute is constantly rejected at the α/ℓ -interface. This solute rejection let gradually to a formation of a solute pile-up ahead of the s/ℓ -interface (known as initial transient) and with that to a concentration increase ahead of the interface and a corresponding decrease of the interface temperature. From the observer point of view the interface recoils as it changes its temperature from liquidus to solidus. Fig. 3b shows the evolution of the microstructure at t = 6912 s (115 min) after initiating pulling. Note that although the α -liquid interface has recoiled by $\Delta z = 310 \,\mu$ m, we show the interface at the same height as in Fig. 3a. Inside the sample the α -liquid interface has moved forward by $\Delta z = 580 \,\mu$ m, whereas the sample had moved backwards by $\Delta z = 890 \,\mu$ m. The following features from Fig. 3b become apparent when compared with Fig. 3a.

 The α-liquid interface is still polycrystalline. It reveals a threedimensionality with grain boundary grooves and an apparent inclination towards the observer, namely in y-direction. It is



Fig. 3. (a) Microstructure at the end of the thermal equilibration (t = 0 s) and (b) after moving the sample under constant conditions for t = 6948 s (116 min) and (c) for t = 12168 s (203 min).

hard to discern whether the highest point of the interface is close to the rear wall or at a position somewhere in the middle of the sample. Due to the observed interface flatness during the homogenization period of 2 h, and as the pulling speed is extremely small ($V = 0.128 \ \mu m/s = 0.46 \ mm/h$) it is quite probable that the isotherms within the samples are flat even when in motion. On the other hand, it is important to notice that the density of NPG is smaller than that of TRIS [18]. As a consequence, the solute pile-up ahead of the s/l-interface reveals an unstable density stratification, which leads to the occurrence of mild but visible convection rolls. This was already reported in a former publication of the authors [23]. For the case of Fig. 3b, this mild convection led to an accumulation of NPG close to the sample walls and thus to a lower liquidus temperature there. This can explain why the interface lags behind at the walls. We will address this topic again in Section 4.3.

- The second interface is still visible in Fig. 3b. It had moved with the sample almost the whole withdrawal distant of $\Delta z = 890 \,\mu\text{m}$, evidently, the growth of this interface is somewhat sluggish. This becomes understandable by the fact that motion of this interface would need an α - β phase transition. The fact that the β -phase, however, grew along the open liquid channels into the α -liquid region will feature in Section 4.2.
- The liquid surrounding the polycrystalline α-phase in Fig. 3a has either vanished or transferred to either liquid channels, round or elongated liquid inclusions (droplets) [26,27]. Channels and droplets at the front (close to the glass wall) are normally well-focused, whereas those in the background are blurry and diffuse. The fact that droplets close to the s/k interface move upwards by thermal gradient zone melting is of sufficient importance (TGZM) [28–31]. However, most of the droplets (either elongated or spherical) simply dissolved with time, as sample pulling carry them into regions of lower temperature where the solubility for NPG of both solid phases is increasing. From the phase diagram it is clear that the droplets are NPG-rich.

Fig. 3c shows the evolution of the microstructure at t = 12168 s (203 min) after initial pulling. The s/ ℓ interface is still polycrystalline. We now observe an interface which is made up of three dimensional hills and grooves. Of importance is the shadowy broad line just below the three dimensional interface. Such a line is also

visible in Fig. 2. As we established, well-focused, migrating droplets that burst by reaching this line, it is apparent that it represents the s/ℓ interface at the front glass walls (the same is of course also conceivable at the rear wall). The fact that the line is shadowy and broad shows that the s/ℓ interface is heavily curved and can thus not be focused well. With the help of the insert in Fig. 4a, the issue shall again be discussed in Section 4.3. Fig. 3c also shows that liquid channels and liquid inclusions have vanished.

The uneven horizontal interface at the lower part of Fig. 3c represents the lower edge of the β band shown in Fig. 3b. From Fig. 3b and c the sample had moved backwards by $\Delta z = 670 \ \mu m$ while the β/ℓ interface had grown upwards by around $\Delta z = 620 \ \mu m$. However, the β - α interface (solid state transformation) did not move faintly.

4.2. Formation of lateral bands

Careful observation of the video sequence, which shows the transition from Fig. 3a and b reveals that the β -phase grew along some of the liquid channels into the α -liquid region until it reached approximately the position of the former second interface at $T_{\rm p}$. After reaching T_{p} , β spread perpendicularly to the sample and thus β -bands form. During the spread of β , we observed both growth into liquid channels and thickening of β -bands by α - β solid state transformation. However, solid state transformation is much slower compared to growth by solidification. In Fig. 3b two β -bands are visible. As they are relatively well-focused, they are located in the front of the sample. Whether the β -bands also spread into the third dimension cannot be determined from our observation. However, the fact that solid state transformation is relatively sluggish leads to the conclusion that while β -bands exist in the foreground, most probably an α solid remains present in the background.

Further proceeding solidification, the α/ℓ interface continued to recoil, so that finally the β -bands reached the α/ℓ interface and formed the new s/ℓ interface. In Fig. 3c, five β grains can be identified that grew into the liquid (labelled with I-V). In fact, most of the solid that can be seen in Fig. 3c is the β -phase solid, which now revealed hardly any (liquid) channels and only a few inclusions. Note that due to the three-dimensionality of the samples, we can only estimate where the grain boundaries in the bulk truly lie.

Moreover, Fig. 3c shows two new bands, now from α -phase, spreading laterally from both side. The origin of these two bands was unfortunately unidentifiable. However, it is obvious that different to the β -phase the α -phase does not grow along liquid channels from areas farther below. In fact, from many experimental observations, it becomes clear that α nucleation occurs far more rapidly than β nucleation, and therefore we attribute nucleation outside the observation window as the possible origin for the α -bands.

Note that the α -bands grew, as did the β -bands, between the existing solid (now β) and the glass wall. The vertical position at which the α -bands appeared correspondly, again, approximately with T_p . Following the occurrence of the α -bands, the β/α interface was partly overgrown by the α -phase and PCG started. Corresponding details will be discussed in Section 4.4.

4.3. Transition between cycles

Fig. 4 shows the development of the s/ℓ interface during one of the repeating cycle of PCG shown in Fig. 2. The first picture was taken at t = 22320 s (372 min) after starting to pull. The time interval between the different pictures is $\Delta t = 600$ s. All pictures reveal a dark s/ℓ interface (labelled with A in Fig. 4a) followed by a grey blurry line some 10 µm behind (labelled with B in Fig. 4a). Both lines are slightly curved in the direction perpendicular to the direction of observation (*x*-direction).

From studies with differently focused samples, it became clear that the blurry line (B) is located close to the front glass wall of the sample. It originates from the s/ℓ interface reaching the front glass



Fig. 4. Sequence of peritectic coupled growth and the transition between cycles.

wall. As we have never managed to clearly focus this line even with different objectives, we conclude that the s/l interface reveals some curvature when approaching the glass wall. As discussed later in this section, this curvature can even be seen by following the shape of a grain boundary (see insert in Fig. 4a). Moreover, 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 it appears that the blurry line might represent two overlaying blurry lines rather than one. From the experience with this organic compound, it is known that neither the α - nor the β -phase is likely to be in direct contact with the glass wall [18]. Obviously, the solid/glass interfacial energy is higher than the sum of the solid/liquid and the liquid/glass interfacial energy. However, in addition to this surface energy argument, it is most likely that - due to the occasionally observable convection – the NPG concentrations at the s/ℓ interface close to the front and rear glass walls are slightly greater (see also observations and discussion in Ref. [23]). This macrosegregation effect also leads to a curved interface, but the resulting curvature is less pronounced compared with that caused by the surface energy argument. Hence, the blurry line labeled with (B) in Fig. 4 primarily originates from the contact problem of either the α - or the β -solid with the wall.

As the microscopic lens had a numerical aperture of 0.1 and thus a depth of field of 55 μ m, the visible vertical boundaries between the two solid phases are located somewhere in the depth of the 600 μ m thick samples, and are neither close nor near a glass wall. This becomes also obvious by the fact that the phase boundaries reaches the top s/ ℓ interface (A) which is supposed to be located some distance away from the glass walls. In Fig. 4a the two bold arrows show examples of lamellae that reaches the top s/ ℓ interface and contribute to its wavy shape. However, as opposed to thin samples with thicknesses of 100 μ m or less, the side-on view observation of the present thick sample does not allow for a clear determination of individual lamellae/liquid interfaces or even triple point configurations.

As the α - and β -phases cannot be distinguish optically, we can only identify them indirectly; a separate observation would be helpful in this case. The PCG interface presented in Fig. 4a shows a minority and a majority phase at the interface. Comparing Fig. 4a with Fig. 4h now reveals two important facts: first, during the course of the cycle, the interface temperature drops by around 0.3 K. The reason for that is a slight concentration shift to a higher NPG concentration in the sample. This is most probably caused by convection and the occurrence of some small macrosegregation (see also discussion in Ref. [23]). Second, the extent of minority phase has increased in Fig. 4h. This can again be understood by a slight increase of NPG, assuming that β is the minority phase. This assumption is also confirmed by the sequence of band formation as discussed in Section 4.2. Therefore, we believe that what we have termed "the secondary phase" in Section 3 is in fact the β -phase. During a cycle it opens like tulip and then erupts into two onion-like objects before nearly disappearing, as shown in Fig. 2.

Fig. 4a also shows three fine lines connecting the top s/ℓ interface (A) with the bottom s/ℓ interface at the front glass wall (B), and they are indicated by transparent arrows. Particularly the fine line on the left confirms the interpretation that the grey, blurred line is caused by the curved s/ℓ interface at the front glass wall as it neatly follows the interface curvature (see insert in Fig. 4a). We interpret these fine lines as grain boundaries separating α -grains. It is important to note that during the course of a cycle these fine lines continue to exist (see arrows in Fig. 4h). It is also evident that those lines seems to originate from the appearance of β -patches. As can be seen in Fig. 4b–c, those patches appear from the top s/ℓ interface (A), and then successively spread over the whole interface. Fig. 4e shows that they grow almost half way down towards the bottom s/ℓ interface at the glass wall (B). Note that at this stage, the amount of vertical phase boundaries has increased substantially, which indicates the increase of the β -phase.

A correlation between these patches and the PCG side view is hardly possible. As in both Figs. 2 and 3 α - and β -lamellae reach up to the top s/ ℓ interface, the interface most certainly consists of α/ℓ and β/ℓ regions. However, due to the three-dimensionality of the sample, corresponding patches at the s/ ℓ interface cannot be seen. They only become visible when growing along the curved interface towards the front glass wall. Then, having spread nearly over the whole interface, these patches suddenly become blurry (Fig. 4f); obviously, they have transformed from flat to uneven objects. Note that this uneven structure correlates with the appearance of onionlike changes of the β -phase noticeable from the side view of Fig. 4g and h. The cycle terminates by the disappearance of bumpiness of the s/ ℓ interface and so Fig. 4h shows a similar situation compare to the beginning of the cycle, Fig. 4a.

An additional detail might also be of importance: the distance between the top s/ℓ interface (A) located in the bulk of the sample and the bottom interface at the front glass wall (B) becomes smaller in Fig. 4e. There it has a minimum magnitude in Fig. 4f, and grows again in Fig. 4g. Thus, the interface curvature in the direction of observation (*y*-direction) decreases slightly, while the β -phase patches transform from flat to bumpy, and decrease again when the amount of β at the interface minimizes shortly thereafter. This observation confirms again that the interface curvature in the direction of observation is not caused by thermal effects.

4.4. First occurrence of isothermal peritectic coupled growth

The transformation from banded structure to PCG is shown in Fig. 5a-h, starting from t = 12276 s to t = 14376 s (205 min–240 min), with a time increment of $\Delta t = 300$ s. Fig. 5a shows that five β grains (labelled with I-V) grew into the liquid, while in the front, two α -bands grew laterally. The pictures were taken directly after the one shown in Fig. 3c. In comparison, Fig. 5h displays the beginning of PCG. It should be noted that three horizontal lines are now visible. As in Fig. 4a, the foremost s/l interface appears dark (labelled with A). Some 10 μ m behind, the s/ ℓ interface line located at the front glass appears as grey blurry line (labelled with B). In addition to these two lines, there exist a wellfocused line in between (labelled with C). This line represents the boundary between the α -phase growing in the front and at lower height and the β -phase growing further in the back and at higher height. Note that the relative positions between lines A, B, and C changed over time. In Fig. 4a which was taken after Fig. 5h line C has moved close to the blurred line A and is thus not directly visible. Note also that in the course of the picture sequence shown in Fig. 5, the β grains I and V meet (see Fig. 5 f and g) and a new grain boundary has formed. In Fig. 5h, this β/β grain boundary is marked with an arrow.

It is important to notice, that the PCG structure visible in Fig. 5h extends across line C. Therefore, the formation of PCG takes place in the bulk of the sample where formerly the β grains grew. From the five grains shown in Fig. 5a, grains II and IV are lagging behind the others.

Fig. 5c and d, illustrate that the two α -bands have amalgamated further grown upwards. The fact that no visible grain boundary between the two α -bands have formed reveal that the two α -bands have the same crystal orientation. Hence it is most likely that the bands have grown from the same origin. In Fig. 5d, the α -phase seems to interact with the β grains II and IV, and in Fig. 5e they



Fig. 5. Transformation from banded structure into peritectic coupled growth.

might have been overgrown by α . Also in Fig. 5d and e it can be seen that α started to grow at the grain boundary of the β grains III and V (indicated by the black arrows). However, in Fig. 5h it can be seen that this α lamella is overgrown by β again. The formation of new lamellae at grain boundaries can also be seen in Fig. 5e and f, indicated by the dotted arrows.

5. Conclusions

The experimental findings presented above can be summarized as follows:

- Holding a sample of hyper-peritectic concentration in a given temperature gradient for 2 h leads to the formation of three regions: a β/ℓ region (probably also with the presence of the α -phase) at temperatures below the peritectic temperature, T_p , an α/ℓ region at temperatures between T_p and the liquidus temperature of the alloy, and fully molten above.
- If this initial configuration moves along a given temperature gradient, with a withdrawal rate smaller than the constitutional stability limit of both solid phases, the α/ℓ planar (polycrystalline) interface recoils while the β -phase grows along liquid channels. At a position close to T_p , β -forms lateral bands in the liquid gap between the α -phase and the glass wall. Marginally sluggish α/β solid transformation was observed.
- When the recoil of the α/ℓ interface reaches the β -bands, the β -phase takes over growth and a flat polycrystalline β/ℓ interface throughout the whole sample grows slightly above the position of $T_{\rm p}$.
- After a while, lateral α-phase bands grow close to a position of *T*_p, now in the liquid gap between the β-phase and the glass wall. The α-band continuous to grow and thus becomes thicker without stopping the β-phase growth in the bulk of the sample. In fact, the α-phase overgrows the β-phase only partially.
- At the beginning of PCG, the s/ℓ interface is curved in direction of observation (y-direction). The highest position is in the bulk and lowest position at the glass walls (definitely at the front but most probably also at the rear glass wall). PCG happens in the bulk at higher positions. It starts forming from a situation where the α-phase grows at a lower position, close to the sample walls, and the β-phase grows at higher positions in the bulk of the sample. Now α grows along the grain boundaries of the β grains, leading to the formation of α patches growing in a β matrix.
- The observed PCG form well-defined cycles of increasing and decreasing phase amounts. From a side-on view, the increase of the amount of β-phase initially resembles tulip-like objects and then the sudden eruption renders onion-like objects before nearly disappearing altogether.
- The mild convection visible in the sample had two consequences. First, the solute concentration at the solid/liquid interface near the tube walls got slightly higher with time compared to the interface at the bulk. This macrosegregation perpendicular to the sample axis let to a curved solid/liquid interface with the highest position in the bulk. Second, with time the average concentration in the liquid part of the sample increased a little. This macrosegregation in sample direction resulted in a slight shift of the corresponding phase amounts.

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