Investigation on the Liquid Flow ahead of the Solidification Front During the Formation of Peritectic Layered Solidification Structures

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Abstract: Several studies have been carried out over the last decades to deepen our understanding of peritectic microstructure formation by using the Bridgman technique. In metals, the formation of layered structures, including bands, island-bands or peritectic coupled growth have been observed post-mortem by analyzing quenched samples. To explain these structures, different theoretical models have been published. Instead of taking metals, organic transparent compounds that show a peritectic region are currently used in this study. This technique provides the advantage of observing in-situ the formation of peritectic morphologies and the dynamics of the solid/liquid interface. Visualizing the flow pattern that occurs during the evolution of the peritectic microstructures represents major progress in this discipline. In order to do so, the organic binary system TRIS-NPG was used as model substance and seeding particles as tracers. It was possible to observe (i) the effect of the mushy zone and its influence on the liquid flow ahead of the solid/liquid interface, for a resting sample, and (ii) the flow pattern during solidification of peritectic layered structures. We found that during the evolution within the mushy zone, an upward movement of liquid through temporarily existing liquid channels into the melt, ahead of the solid/liquid interface takes place. Thus, during solidification, the solutal-buoyancy-driven flow pattern that forms in front of the solid/liquid interface is occasionally interrupted by fine upward flows, called micro-plumes. On the one hand, the formation of banded structures is favorable, since the peritectic phase grows via the existing liquid channels within the initial primary phase. Whereby, the formation of the peritectic layered structures seems to be not influenced by the micro-plumes. On the other hand, the spreading of the primary phase in a lateral direction along the solid/liquid interface of the just-formed peritectic phase is probably hindered by micro-plumes.

Introduction

Within the peritectic region and close to the limit of constitutional undercooling, the primary phase and the peritectic phase can form layered structures [1] like bands, island bands, and peritectic coupled growth (PCG). Such complex structures were found in metals [2-8], whereby, the author investigated [9-16] the dynamic of formation on layered peritectic microstructures by using the binary transparent organic model system TRIS-NPG [17]. Such model substances display a high-temperature non-faceted phase, called plastic crystal. Which solidify similarly to metals. Additionally, the use of transparent substances enables an in-situ observation of the solid/liquid interface dynamic during the formation of peritectic layered patterns. Therefore, it was possible to observe competing growth in the form of oscillating, non-planar coupled solidification structures of the primary and peritectic phases. It has also been shown that layered structures in form of bands lead to PCG. This is due to varied growth of both phases or by multiple nucleation at the solid/liquid (s/l) interface. Since this morphology is highly influenced by thermo-solutal convection, corresponding micro-gravity (μg) experiments, organized by ESA, will be done aboard the ISS 2019.

In this paper, the influence of thermo-solutal convection on the formation and growth of peritectic layered structures on earth was studied.

Experimental Set-up

Directional solidification was carried out by using the Bridgman technique. The cooling and heating zone consisted of brass plates, with a guide for a glass sample, encased by a ceramic cover. The temperature in both zones was selected in such a way that the s/l interface is visible within the adiabatic zone. Rectangular glass samples were pulled vertically with a constant velocity PC-controlled through the temperature gradient of G_T=5.6 K/mm within the adiabatic zone. The sample was illuminated through the adiabatic zone to observe the forming solidification morphology with a light transmission microscope and every 30 seconds pictures were recorded by a CCD camera for a subsequent evaluation.

For visualization of the flow pattern seeding particles were used, in the form of hollow glass spheres HGS [18] with an average distribution size of 2–20 μm. The material density was similar but a little bit larger compare to the melt density; this ensures that the seeding particles approximately follows the flow.

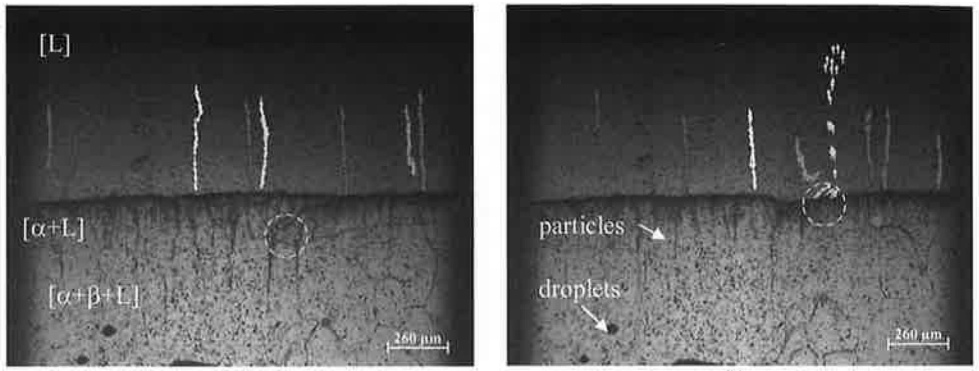
The peritectic model system consists of the two organic substances TRIS and NPG which were obtained as a powder. NPG has the lower melting point and about 20% lower density than TRIS. NPG, with a purity of 99%, and TRIS with 99.9^{+} % were used as delivered and alloys within the peritectic concentration ($0.47 \leq x \leq 0.54$ mol fraction NPG) were prepared within a glove box under an argon atmosphere. The preparation was carried out by mixing in the solid state and homogenization by melting and cooling, respectively. Finally, the alloy was ground to a powder and mixed with HGS particles. The rectangular quartz tubes (100 x 2000 μm^2 cross sectional area, 100 μm glass wall thickness) were filled with the organic alloy by capillary force and sealed with an UV-hardening glue. More details of the preparation are given in detail in [16]. The glass sample was placed into the furnace and pulled up at 2000 μm/s in order to homogenize the alloy concentration within the sample. After remaining stationary for 1 h to reach a state of thermal equilibrium, the sample was pulled down at a constant rate of $0.12 \leq V_P \leq 0.21$ μm/s.

Results and Discussion

Micro plumes: The evolution of the solid and liquid phase within the mushy zone was investigated for a concentration of $x = 0.54$. After one hour at rest within the temperature gradient, thermal stability was reached and the s/l interface showed a planar front. The seeding particles' motion in the melt and the dynamics of liquid droplets, channels and grain boundaries within the mushy zone, where the phases α, β and liquid coexist, was observed for 27030 s (7.5 h). During this time, the particles sediment due to their slightly higher density following the gravitational force with $v = 0.66 \pm 0.11$ μm/s. The motion of a few selected individual particles ahead of the s/l interface is visualized by arrows (Fig. 1a), whereby, each arrow represents the alteration of the position within 30 seconds. Once the particles have reached the interface, they accumulate and in particular, they remain unmoved, which highlights the structure of the solidification front, channels, and cracks.

In contrast to the precipitation of the particles, a temporary localized upward movement was observed, as highlighted in Fig. 1b, marked with yellow arrows. Particles were detected, indicating which stream flows upwards from the s/l interface into the liquid in form of a micro-plume. Carefully conducted investigations of the corresponding picture sequences uncover the fact that the particles were initially trapped in a liquid pocket within the solid, shown as a yellow circle in Fig.1a.

Observations indicate that the upward movement of the particles in the melt causes a local flow noise, recognizable by the change in the direction of the blue arrows, see Fig. 1b. In addition, two grain boundaries (red and green dots) are marked to exhibit the migration by solidification and melting within the three phase region α, β and liquid. It can be seen that the migration velocity depends on the position within the mushy zone.



(a) (b)

Figure 1. Visualization of particle motion in a sample at rest by coloured arrows. The yellow circle marks a liquid pocket and the red and green dots triple points. (a) Time frame is from 810 to 1610 s and (b) from 1650 to 2460 s.

It is important to note that the mushy zone was formed by fast solidification with elongated fine dendrites and corresponding interdendritic liquid. After homogenization a coarse grain structure with traces of the former interdendritic liquid that looked like small channels can be seen. According to the phase diagram the enclosed liquid in the still existing interdendritic liquid is enriched on NPG. Due to the migration of the grain boundaries in the temperature gradient, such high NPG-enriched channels got occasionally connected to the s/l interface. Due to the lower density of NPG-enriched liquid, those 'open' channels tends to form micro-plumes with rising flow along the channel towards the melt.

Layered structures: The formation of layered structures in the form of bands and the subsequent alteration into a PCG is described in detail for $x = 0.52$ and pulling velocity $V_p = 0.174$ μm/s. In order to better recognize the effects that occur during solidification, an explanatory sketch is attached below the picture (Fig. 2). Initially, there are two solid phases present: the primary α-phase which forms the planar s/l interface, and at a lower temperature level, the β-phase and eventually remaining α-phase, (see Fig. 2a). Ahead of the interface, thermosolutal convection showed a downward movement in the center and a corresponding upward motion along the side walls of the sample (red arrows, Fig. 2a). For solidification rates where phases grow in a planar manner, both interfaces try to reach stable growth conditions at the corresponding solidus temperature, and the s/l interface of the α-phase started to recoil. The interface of the metastable β-phase was frozen and followed the pulling velocity of the sample until the s/l interface of the α-phase passed the initial temperature level of the β-phase. Here, the β-phase grew through small liquid channels located in the α-phase close to both glass walls up to the s/l interface. Since the mushy zone is within a temperature gradient, a series of complex processes occur. The microstructural evolution is associated with melting and re-solidification of grain boundaries and migration of liquid pockets. Temporarily, additional liquid channels form by connecting 'wet' grain boundaries and/or liquid pockets to the bulk melt. If feeding though a 'wet' grain boundary network or a network of liquid pockets is possible, NPG-enriched liquid rises upwards through the liquid channels towards the melt forming micro-plumes, like the one shown in Fig. 2b. This plume originated in a liquid channel in the length of approx. 1500 μm deep into the solid phase. At this temperature level only concentrations close to pure NPG are liquid. Although, a slight fluctuation of the new formed β/l interface was observed, no direct influence on the peritectic band could be detected. However, both effects induced a new convection pattern in the melt, with an upward movement slightly offset from the center and a downward movement along the sidewall of the glass tube.

While β is the preferred solidifying phase it spreads out from the side glass wall along s/l interface of the α phase toward the center. During the growth of the peritectic phase on both side, the micro-plume on the left part is still active (Fig.2c). Shortly before the two β-phase bands were combined in the center, the primary α-phase became the preferred phase again (Fig. 2d). This can be seen by the fact that the α-phase expands in a lateral direction, forming the growing triangle shown in Fig. 3a.

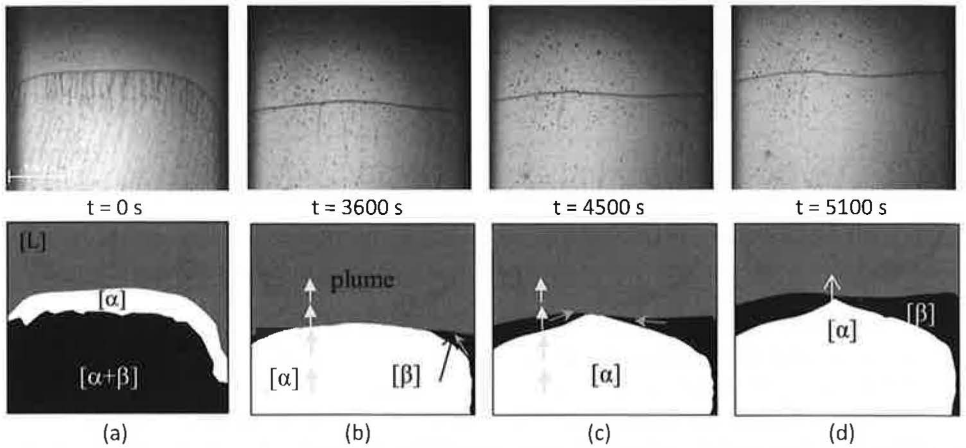


Figure 2. Formation of two β island bands unaffected by the liquid flow of a NPG enriched plume (yellow arrows). The black dots in the pictures are the seeding particles and the red arrows shows the thermosolutal convection in front of the s/l interface.

Additionally, Fig. 3b shows a newly occuring α-phase on the right side of the sample. The phase seems to have originated by nucleation at the β/l interface close to the wall. However, a precise determination is not possible. As the primary phase grew along the s/l interface in all directions, two events that initiate the transition to PCG were observed: the micro-plume to the left of the center of the sample and the transition of the new α interface from planar to cellular growth on the right side of the image (Fig. 3c). The growth of the primary phase from the center to the left edge was stopped as the α-phase came into contact with the micro-plume. Unlike the spread of the peritectic phase, here, the flow prevented the lateral growth of the α-phase. This is attributed to the influence of the NPG enriched liquid.

Different to the previously described formation of the two β-island bands, the following can be observed here: (i) At the right side of the sample, the growth in the lateral direction initially did not take place in the full depth of the sample. Rather, a growth of the band near the front and rear glass walls was seen. Furthermore, it seems that this was followed by a partial phase transformation from the existing β phase to the α phase. (ii) The newly formed α/l interface changed from planar to cellular growth. At the same time, the preferred phase changed from the primary to the peritectic one, also shortly before both α island bands linked up. This led to a PCG (Fig. 3d), which finally developed into stable dendritic growth of the α-phase. (iii) On the left side of the sample, the micro-plume halted the growth of the α-phase, and β remained the preferred phase. The solidification structure remained planar on the left side and on the right α and β grew in a PCG manner. As soon as the α-phase became the ultimately preferred phase on the right side, the entire solidification morphology was dendritic (not shown here).

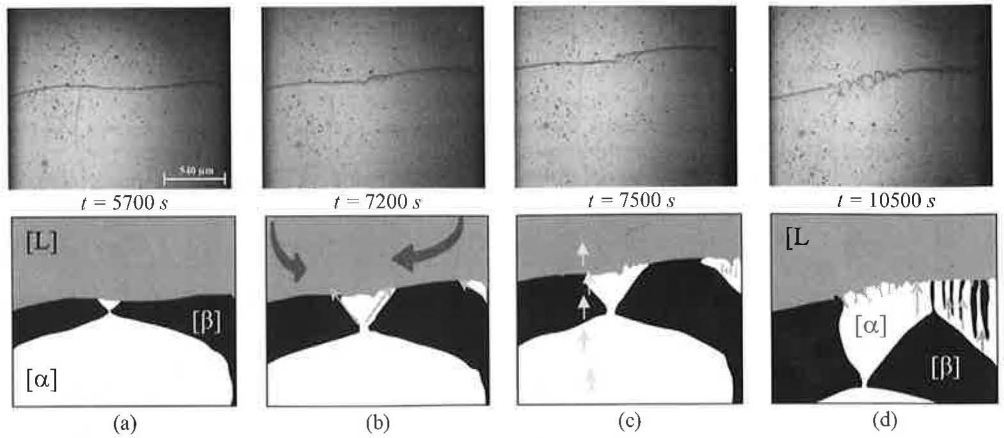


Figure 3. Transformation from banded layered structures to peritectic coupled growth. (a) Shortly before both β-island bands are joining together the α-phase is the new preferred phase. (b) Additionally, the α-phase forms a new band coming from the right side. The new band solidifies in a planner manner before the s/l interface becomes unstable and cellular growth occurs (c). The lateral growth of the α-phase growing at the center is stopped on the left side by a liquid channel/micro plume. (d) Within the intercellular liquid of the cellular α-phase the β-phase grows and peritectic coupled growth is formed.

Conclusions

Peritectic systems show a multitude of layered solidification morphologies at the limit of constitutional undercooling. Such structures are strongly influenced by thermosolutal convection, which is always present on Earth due to the influence of gravity. Solidification experiments were carried out with the transparent peritectic model system TRIS-NPG under 1g conditions. Further experiments are planned under μg one aboard the ISS in 2019. In order to visualize the thermosolutal convection flow for experiments under 1g conditions, seeding particles were added to the organic substances as tracers.

The investigations show a visible influence on the layered structures by the formation of a micro-plumes which has its origin in the former mushy zone of the primary and peritectic phase. The solid is interspersed with melt of lesser density in form of droplets and channels which has it origin in the former interdendritic liquid. Migration movements in the solid form small liquid channels, which leads to the development of micro-plumes. Interestingly, the formation of two β-island bands in combination with the existing micro-plume changed the flow pattern of the thermosolutal convection in the melt ahead of the s/l interface. Despite of the convection occurring in the bulk melt, the formation of peritectic coupled growth was observed.

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