

In Situ Observation of Coupled Peritectic Growth

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Abstract

Several studies on directionally solidified and quenched samples have shown that coupled lamellar growth does not only occur in eutectic but also in peritectic systems. However, the condition at which such unusual growth form for peritectics occurs is unclear. By using a transparent $\text{Ni-Ni}_3\text{Al}$ peritectic compound in situ observations of the initialisation of coupled lamellar peritectic growth were made. We found that this growth form can be obtained either by (i) reducing the growth velocity from above the critical value for morphological stability of both solid phases to a value below, or by (ii) long-time growth with a constant velocity below the critical value for morphological stability of both solid phases. The latter happens via island banding, where nucleation and lateral growth of the peritectic phase compete with growth of the primary phase. Interphase spacings and the widths of α and β lamellae were measured as function of growth velocity for a fixed composition and as function of composition for a fix growth velocity.

1. INTRODUCTION

A peritectic equilibrium is very common for many daily-life alloy systems like steel, bronze, high T_c superconductors and rare earth permanent magnets [1]. It is characterised by the fact that liquid (L) and primary α phase form an invariant equilibrium with the peritectic β phase. Close to or below the limit of constitutional undercooling of both solid phases wide spectrums of complex microstructures have been found in different peritectic systems [2-19]. Examples are isothermal peritectic coupled growth (PCG), cellular peritectic coupled growth, discrete bands, island bands and oscillatory tree-like structure. It is especially the observation of two-phase growth, either coupled or banded, which has drawn the recent attention of researchers to this field [10-11,15,17,20-22].

Dobler et al. suggested as a necessary condition for isothermal PCG to occur that the ratio between thermal gradient G and growth velocity V must be close to or above the critical value for morphological stability of the primary phase [11]. They also found that lamellar PCG can be stable even though the slope of the undercooling-spacing relationship is negative and that the stability of PCG is limited at both small and large spacings by short-wavelength oscillatory instabilities. From their experimental finding they concluded that lamellar isothermal coupled growth should be observed in a limited domain of the two-phase range between C_α and C_β when two conditions are satisfied.

Firstly, the phase with the larger solute rejection should be morphologically stable. Secondly, the spacing of the composite structure should fall inside a stable range of spacings that is bounded by short wavelength ($1 - \lambda$) oscillatory instabilities. These conditions are necessary but not sufficient to obtain isothermal peritectic coupled growth.

Another prerequisite is the initiation of the coupled structure [10]. Either the isothermal coupled growth is initiated by island banding (as observed in [11]) or by a morphological instability which occurs during the rapid lateral growth of the secondary phase on the primary phase similar to that observed with eutectic [23]. However, the latter mechanism has not been proved experimentally so far.

In the present paper experimental investigations of the initiation of PCG are presented. They were gained by performing in situ observations of the transparent organic non-faceted/non-faceted (nf/nf) peritectic TRIS-NPG system. TRIS is the abbreviation for Tris(hydroxymethyl)aminomethane and NPG for Neopentylglycol. The fact that this organic compound solidifies with two disordered solid phases which reveal a peritectic in an intermediate concentration range makes studies on this system suitable for comparing with corresponding phenomena in metallic systems. The TRIS-NPG phase diagram was published by Barrio et al. [24] and shows a peritectic equilibrium at $T_p = 410.7$ K with $C_\alpha = 0.47$ mol.% NPG, $C_\beta = 0.515$ mol.% NPG, $C_L = 0.54$ mol.% NPG.

2. EXPERIMENTAL PROCEDURE

The organic substances TRIS and NPG were purchased from Aldrich [25] with an indicated purity of 99 % and 99.9+ %, respectively. Both compounds are reported to be highly hydroscopic [26]. In accordance with the material preparation published in [24,30-31], the water content of NPG was reduced by keeping the material in a dry atmosphere at 310 K for 24 hours. TRIS was used as delivered. Different types of sample geometries and sealing substances/procedures were tested. Due to the relatively high hot zone temperature necessary for peritectic solidification experiments many of the tested sealing materials such as UV hardening and silica-based glues started leaking after some hours. The best results were obtained using large rectangular tubes (2000 x 100 μm inner dimensions and 100 μm wall thickness [27]) with glued ends. The alloy and sample preparation was performed within an Argon-filled glove box. The humidity within the glove box was reduced to below 10^4 ppm and the oxygen content below 2×10^3 ppm, estimated with a hygrometer and an air oxygen measuring device. For the preparation of the different alloy compositions the pure substances were weighed and joined in small glass containers which were closed with plastic caps afterwards. Next, the glass container was heated on a hot-plate until the organic powder melted, then it was shaken to improve the mixing and then slowly solidified (~ 1 hour). This procedure led to a refinement of the alloys because impurities with a boiling temperature lower than the organic powder (e.g. water) should have condensed on the cap of the glass container [30-31]. A similar refining procedure of the hygroscopic NPG was reported by Barrio et al. [24]. When the alloy was fully solidified, the glass container was crushed and the waxen alloy was ground and filled into a new storage container. From this container small amounts of the alloy were taken to fill the rectangle glass tubes.

For the filling, the rectangular glass tubes were laid on a hot-plate such that one side was on the plate and the other side protruded freely. Small amounts of the alloy were deposited on the hot-plate next to the open side of the tube. As soon as the alloy melted, the liquid was dragged into the tube by capillarity until it reached the colder side of the tube where it solidified. This procedure ensured that enough room for expansion due to melting (and heating) was left free. Next, the tube was slowly dragged off the hot-plate allowing the material to solidify and then both ends were sealed. During the investigations in the Bridgman furnace, both ends of the tubes were outside of the Bridgman furnace and so kept around room temperature, so that the solid alloy further sealed the liquid part of the tube.

The Bridgman furnace consisted of a cold and a hot copper block with a distance of 4 mm [30-31]. The hot zone block was heated to a temperature of 453 K using an electric resistance heater, the cold zone temperature was controlled by a water circuit and set to a temperature of 353 K. The temperatures on both sides were measured with Pt 100 temperature sensors placed inside the copper blocks and regulated independently with an accuracy of ± 0.1 K. The temperature gradients were measured with a 200 μm NiCr-Ni thermocouple within a filled large rectangular sample (2000 μm x 200 μm inner dimensions and 100 μm wall thickness [24]). The measured gradient $G = 14.2$ K/mm was linear within the adiabatic/observation zone. The microscope was equipped with a CCD camera and self-developed software allowing the recording and storage of images and temperature data with a frame rate of up to 10 images per second. Furthermore, the software allowed the measurement of positions in the field of view.

3. RESULTS AND DISCUSSION

In order to get an isothermal PCG we used different hypo-peritectic alloys ($C_\alpha < C_0 < C_\beta$), and different growth velocities. The temperature gradient was kept constant. As a matter of fact we were able to achieve the isothermal PCG by two different ways: (i) reducing the growth velocity from above the critical value for morphological stability of both solid phases to a value below, and (ii) by long-time growth with a constant velocity below the critical value for morphological stability of both solid phases.

3.1. PCG by Reducing the Growth Velocity

Figure 1 shows the resulting transition from simultaneous growth of α dendrites ahead of β cells to isothermal PCG for a hypo-peritectic alloy with $C_0 = 50$ mol.%. The pulling speed was reduced from 0.64 $\mu\text{m/s}$ down to 0.19 $\mu\text{m/s}$. The transition took around 900 s which corresponds to a sample displacement of 90 μm . Note that the two different solid phases are optically indistinguishable. However, by experience based on phase diagram information and on several observations for different alloy concentrations and growth velocities the two phases can be differentiated indirectly.

The starting point to get an isothermal PCG by growth velocity reduction is that an array of leading α dendrites (or cells) is followed by an array of β cells (both arrays grow at different depth in the sample). For hypo-peritectic alloys of the TRIS-NPG system this is typically the case if the growth velocity is above the critical value for morphological stability of the α phase [32].

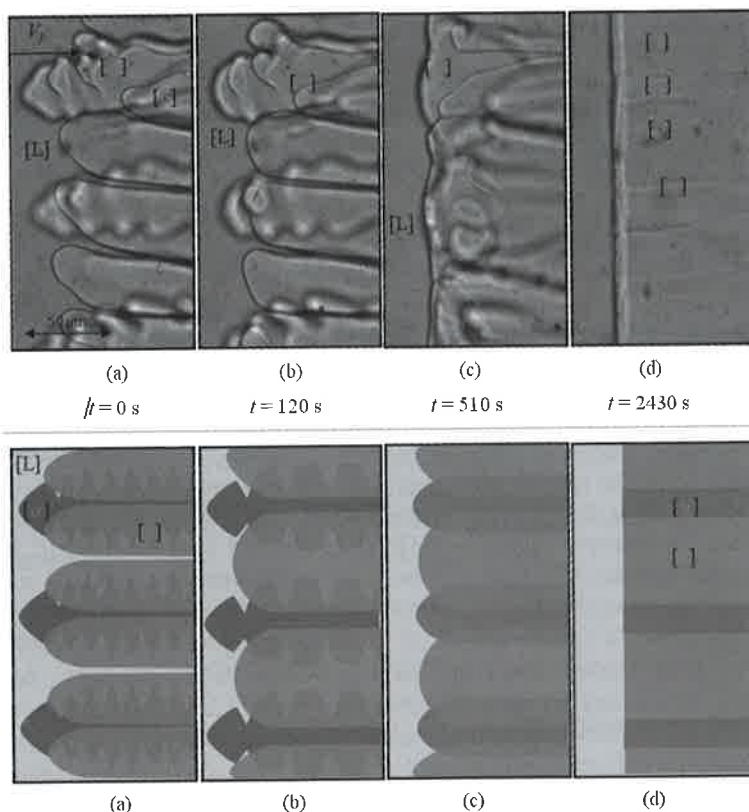


Figure 1. Formation of PCG by reducing the pulling velocity from $0.64 \mu\text{m/s}$ down to $0.19 \mu\text{m/s}$ for a hypo-peritectic alloy with $C_0 = 50 \text{ mol.\% NPG}$. As the initial state an array of α dendrites grew ahead of (and behind) an array of β cells.

Starting from an array of α dendrites (or cells) ahead of an array of β cells a velocity reduction leads to a significant coarsening of the morphologies so that both solid arrays form more or less planar solid/liquid interfaces which are located side by side at different depths in the sample (Figure 1c). Now, the optical differentiation of the two solid phases is really hard. However, from carefully studying the corresponding sequence of pictures the following observations could be made: At distinct positions α grows perpendicular to the pulling direction towards β so that the nearly planar L/ β interface starts to reveal pockets filled with α . These pockets are the origin of the α lamellae. Finally when isothermal PCG is fully established there exists only one solid/liquid interface throughout the depth namely parallel α and β lamellae orientated in growth direction.

In the experiment presented in Figure 1 the interphase spacing could be estimated to be $\lambda = 99 \pm 9 \mu\text{m}$. The variation of $\pm 9 \mu\text{m}$ is due to the fact that different lamellae reveal different spacings. The thickness of the α lamellae could be estimated to be $\lambda_\alpha = 72 \pm 7 \mu\text{m}$

and that of the β lamellae to be $A_\beta = 27 \pm 2 \mu\text{m}$. The A_β/λ ratio which represents the volume fraction of β in the present configuration is 0.27 ± 0.04 , which is in good agreement with the position of C_0 within the peritectic interval ($C_\beta - C_\alpha$). Note that the value is similar to the theoretical limit of 0.28 for rod-like growth in coupled eutectic growth. However, due to the transparency of both solid phases it is difficult to distinguish between fibres and lamellae from the present pictures.

3.2. PCG by Banding in Combination with Nucleation

Isothermal PCG initiated by banding in combination with nucleation was observed for several alloys with hypo-peritectic compositions ($C_\alpha < C_0 < C_\beta$), namely $C_0 = 0.48, 0.50$ and $0.51 \text{ mol.}\%$. Figure 2 shows the dynamics of band formation. For a growth velocity below the critical value for morphological stability of both solid phases, each of the two solid phases tries to grow with a planar solid/liquid interface. If a planar solid/liquid interface is made by one of the two solids, the second will probably nucleate during the formation of the solute pile-up ahead of the first and then spread along the interface until it covers the whole interface. As first shown by Boettinger [28] and later analysed by others [29] this process also happens vice versa leading to alternation of bands perpendicular the interface, the so-called banding.

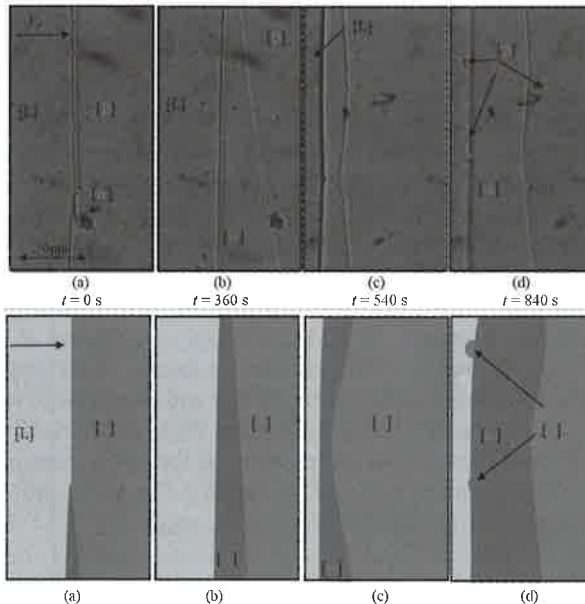


Figure 2. Dynamics of band formation. The pre-existing planar L/ β interface is overgrown by α . Later β nucleates again at the L/ α interface. The observation was made for a hypo-peritectic alloy with $C_0 = 0.51 \text{ mol.}\%$ and a pulling velocity of $0.1 \mu\text{m/s}$. Note that the microscope table has been moved from picture (b) to (c).

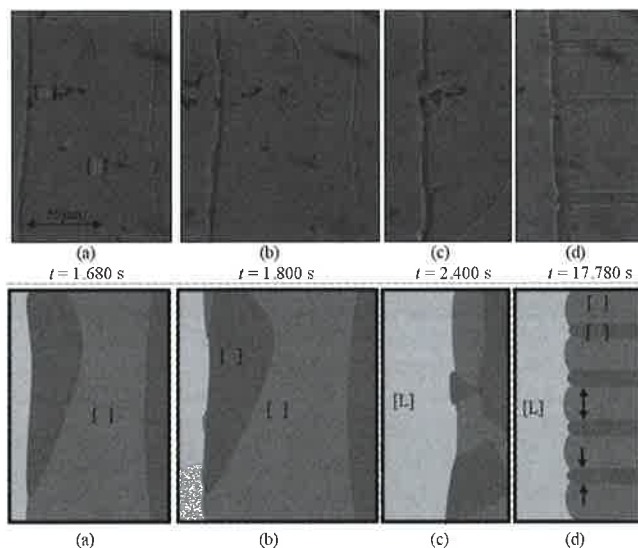


Figure 3. Initiation of PCG from island banding. Successive nucleation and growth of α and β in the form of island bands leads to the formation of PCG. The pictures were taken in direct continuation of the sequence shown in Figure 2.

Although optically indistinguishable the two different solid phases can be differentiated indirectly by experience based on phase diagram information, on several observations for different alloy concentrations and growth velocities, and on careful observations of the dynamics of changes. Our in situ study of the transformation from discrete bands to isothermal PCG starts by an overgrowth of a planar L/α interface by the peritectic β phase. The planar β solidification front grows stably until the primary α phase nucleates again at various positions at the L/β interface. Now the lateral growth of α competes with the forward growth of β . During this competition β also nucleates at various positions at the L/α interface. This situation is known as the stage of island bands (see Figure 3c). With a suitable nucleation frequency and an adequate ratio of lateral and forward growth of the two solid phases, isothermal PCG establishes within around 20 minutes (Figure 3d). Corresponding to the position of the alloy concentration within the peritectic plateau ($C_\alpha = 0.47 \text{ mol.}\% < C_0 = 0.51 \text{ mol.}\% < C_\beta = 0.515 \text{ mol.}\%$) the width of β lamellae, λ_β , is large and that of the α lamellae, λ_α , is small.

3.3. Lamellar Spacings

In most cases the α and β lamellae that occur during isothermal PCG were parallel and straight. In only a few cases, short wavelength oscillatory instabilities, which are reminiscent to $1 - \lambda$ instabilities, occur. However, no systematic studies on this topic have been made so far.

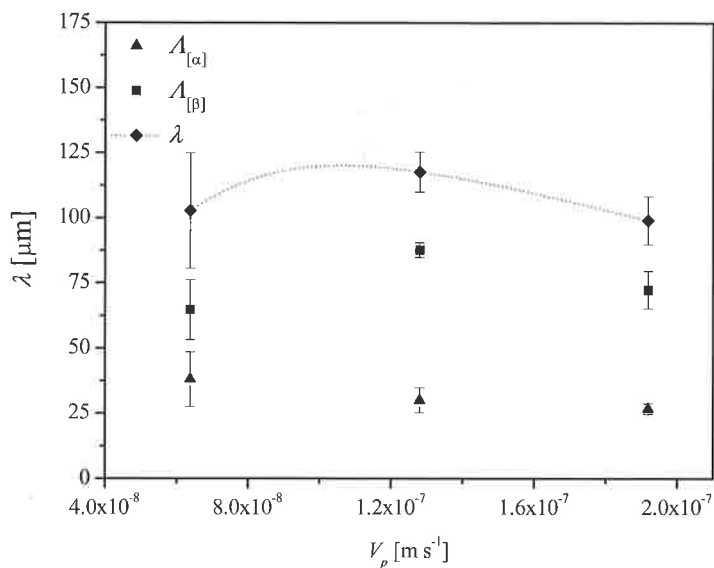


Figure 4. Measured averaged interphase spacing, λ , and width of α and β lamellae, A_{α} and A_{β} , as functions of growth velocity for $C_0 = 0.50$ mol.% NPG.

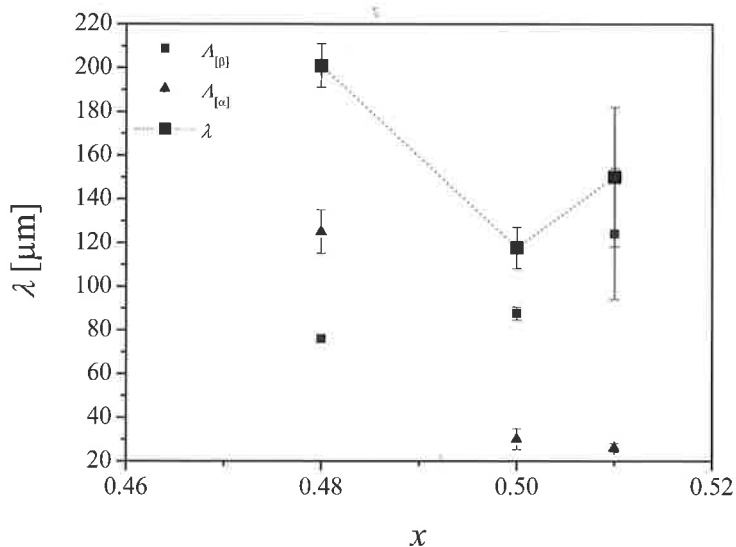


Figure 5. Measured averaged interphase spacing, λ , and width of α and β lamellae, A_{α} and A_{β} , as functions of concentration for a growth velocity $V = 0.1 \mu\text{m/s}$.

Although the optical impression of the width of a lamella depends to some extent on the focus depth of the microscope, the width of the α and β lamellae as well as the interphase spacing has been estimated in an averaged way for different moments in time and at different positions. In Figure 4 the interphase spacing and width of α and β lamellae are shown as functions of growth velocity for a hypo-peritectic concentration $C_0 = 0.5$ mol.% NPG. From eutectic solidification it is known that the interphase spacing increases with decreasing growth velocity. Our measurements suggest that this might be different for peritectic solidification. Although the error bar at $V = 0.07 \mu\text{m/s}$ is quite large the decrease in λ for smaller growth velocity seems significant. In Figure 5 the interphase spacing and width of α and β lamellae are shown as functions of concentration for $V = 0.1 \mu\text{m/s}$. Obviously, the interphase spacing reveals a minimum at a concentration of around $C_0 = 0.5$ mol.% NPG.

Finally, it is worth mentioning that the ratio of lamella width to interphase spacing is in good agreement with the position of C_0 within the peritectic interval ($C_\beta - C_\alpha$).

4. CONCLUSIONS

As presented in this work, direct in situ observations of the formation of isothermal PCG were possible by using a transparent nf/nf peritectic alloy. We found that isothermal PCG can be obtained by two different ways: (i) reducing the growth velocity from above the critical value for morphological stability of both solid phases to a value below, and (ii) by long-time growth with a constant velocity below the critical value for morphological stability of both solid phases i.e. via island bands. For both cases observations of the dynamics of the formation of isothermal PCG are provided. The ratio of lamella width to interphase spacing is in good agreement with the position of C_0 within the peritectic interval. However, we have presented experimental results that suggest that the interphase spacing in isothermal PCG might reveal a maximum at a certain growth velocity rather than increasing further with decreasing velocity.

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REFERENCES

- [1] Kerr HW, Kurz W. *Int Mater Rev* 1996;41:129.
- [2] Vandyoussefi M, Kerr HW, Kurz W. *Acta Mater* 1997;45:4093.
- [3] Hunziker O, Vandyoussefi M, Kurz W. *Acta Mater* 1998;18:6325.
- [4] Karma A, Rappel WJ, Fuh BC, Trivedi R. *Metall Trans A* 1998;29:1457.
- [5] Tokieda K, Yasuda H, Ohnaka I. *Mater Sci Eng A* 1999;262:238.
- [6] Vandyoussefi M, Kerr HW, Kurz W. *Acta Mater* 2000;48:2297.
- [7] Yasuda H, Notake N, Tokieda K, Ohnaka I. *J Cryst Growth* 2000;210:637.
- [8] Kohler F, Germond L, Wagnière JD, Rappaz M. *Acta Mater* 2000;57:56-68.
- [9] Trivedi R, Park JS. *J Cryst Growth* 2002;235:572.

- [10] Lo TS, Dobler S, Plapp M, Karma A, Kurz W. *Acta Mater* 2003;51:599.
- [11] Dobler S, Lo TS, Plapp M, Karma A, Kurz W. *Acta Mater* 2004;52:2795.
- [12] Trivedi R, Shin JH. *Mater Sci Eng A* 2005;413-414:288.
- [13] Lograsso TA, Fuh BC, Trivedi R. *Metall Trans A* 2005;36:1287.
- [14] Liu S, Trivedi R. *Metall Trans A* 2006;37:3293.
- [15] Su YQ, Luo LS, Li XZ, Guo JJ, Yang HM, Fu HZ. *Appl Phys Lett* 2006;89:2319181.
- [16] Luo LS, Su YQ, Guo JJ, Li XZ, Fu HZ. *Sci China Phys Mech Astron* 2007;50:442.
- [17] Luo LS, Su YQ, Li XZ, Guo JJ, Yang HM, Fu HZ. *Appl Phys Lett* 2008;92:0619031.
- [18] Luo W, Shen J, Min Z, Fu H. *J Cryst Growth* 2008;24:5441.
- [19] Luo WZ, Shen J, Min ZX, Fu HZ. *Mater Lett* 2009;63:1419.
- [20] Busse P, Meissen F. *Script Mater* 1997;36:653.
- [21] Lee JH, Verhoeven JD. *J Cryst Growth* 1994;144:353.
- [22] Li Y, Ng SC, Jones H. *Script Mater* 1998;39:7.
- [23] Akamatsu S, Moulinet S, Faivre G. *Metall Mater Trans A* 2001;32:2039.
- [24] Barrio M, Lopez DO, Tamarit JL, Negrier P, Haget Y. *J Mater Chem* 1995;5:431.
- [25] <http://www.sigmaaldrich.com>.
- [26] <http://fscimage.fishersci.com> search for 126-30-7 and 77-86-1.
- [27] <http://www.vitrocom.com>.
- [28] Boettinger WJ. *Metall Trans* 1974;5:2023.
- [29] Trivedi R. *Metall Mater Trans* 1995;26A:1583.
- [30] Mogeritsch J, Ludwig A, Eck S, Grasser M, McKay B. *Script Mater* 2009;60:882.
- [31] Mogeritsch J, Eck S, Grasser M, Ludwig A. *Mater Sci Forum* 2009;649:159.
- [32] Ludwig A, Mogeritsch J, Grasser M. *Trans Indian Inst Met* 2009;62:433.