In-situ observation of eutectic growth during directional solidification of Succinonitrile - (D)camphor- Neopentyl glycol alloys under imposed velocity transients

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Abstract

In the present work are reported ground-reference results from a series of transient solidification experiments with the organic eutectic alloys SCN-23.6 DC (wt.%) and SCN-24.2DC-0.5NPG (wt.%), which have been performed in preparation of microgravity experiments using a new multi-user facility called Transparent Alloys or DIRSOL. In 1g lab conditions we investigated the response of rod-like eutectic patterns to imposed transients, involving defined acceleration and deceleration of the growth velocity. The patterns have been recorded in-situ in oblique view using a long distance optics and were analysed for a region of interest of 640 µm x 320 µm over long periods of time. The time dependent growth velocity and the associated acceleration / deceleration were determined using images from a side-view camera.

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The reported results mainly refer to the spacing distribution and the hexagonal order parameter S_0, dynamically attained at a defined time instant, i.e. at the moment when the local growth velocity reaches V = 40 nm s^{-1} along deceleration 80 → 10 nm s^{-1} or acceleration 10 → 80 nm s^{-1} paths. The major result is that the hexagonal order is deteriorating under transient growth conditions compared to steady state conditions. We could not observe an increase of order for either imposed acceleration or deceleration, mainly because spacing adjustment is accomplished by abrupt morphological transitions which destroy the previous order.

The abrupt morphological transitions are clearly identified as sharp events along an experiment cycle 80 → 10 → 80 nm s^{-1} and could conveniently be seen in hysteresis loop diagrams. Upon deceleration the abrupt spacing adjustment event corresponds to a transition from fibrous to vermicular morphology. Upon acceleration the abrupt spacing adjustment event corresponds to spontaneous rod splitting.

Key words: Transparent alloy; Optical microscopy; Eutectic solidification; Solidification microstructure; Spacing selection; Order–disorder phenomena

1. Introduction

The binary and ternary transparent organic succinonitrile–(D)camphor–neopentyl glycol (SCN-DC-NPG) alloys emerged as excellent model systems for studying univariant and invariant eutectic growth. They show lamellar or rod-like eutectic structures, depending on the alloy composition [1-4]. The rod-like patterns resulting from coupled growth in the binary near-eutectic SCN-DC alloy were investigated in real-time in both thin

and thick samples [4, 5]. In samples of about 400 μm thickness processed for different values of the pulling velocity *V* over several hours each it was found [5] that the rod-like pattern displays hexagonal order while containing a large number of topological defects. The average rod spacing λ_{av} reaches a constant value and scales approximatively as the -1/2 power of *V*, being close to the minimum-undercooling value λ_m^{JH} given by the Jackson-Hunt model [6] for rod-like patterns. Interestingly, authors of [5] stated that the long-range order of the rod-like pattern increased when the pulling velocity *V* increased, an observation that was reported earlier by Ratke and Alkemper [7] for the Al-Al_3Ni eutectic. However, this was not a general behaviour but depended on the applied velocity-time (*V-t*) profile. There is thus a need to perform controlled transient experiments to better understand the dynamics of the rearrangement processes in a eutectic pattern in response to changing growth velocities. Large-scale parallel phase-field simulations have already been performed in this respect [8] for a rod-like eutectic. The simulation results demonstrate that the ordering rate of the pattern is directly correlated to the applied *V-t* profile, and hence to the history of the process. Authors of [8] reported that deceleration of the velocity improves the degree of hexagonal order whereas an acceleration results in a mixture of lamellae and rods. This is in contradiction to [5] and [7]. In fact [7] suggested that deceleration will necessarily imply local rod elimination processes and hence increase disorder, while acceleration would tolerate spacing distributions above the minimum undercooling spacing without rod splitting events. It was Perrut et al. [9] who provided a quantitative analysis of the threshold spacing for rod splitting and rod elimination. His analysis showed that the threshold spacing λ_{sp} for rod splitting obeys a $V^{-1/2}$ scaling law with $\lambda_{sp}/\lambda_m^{JH} \cong 1.2$ while the rod elimination threshold spacing λ_{el} exhibits a large

deviation from the $V^{-1/2}$ scaling law, more pronounced at low values of V and termed "overstabilty".

On this background we engaged in preparing a series of transient solidification experiments with distinct acceleration and deceleration profiles to be performed in a new multi-user facility called Transparent Alloys (TA) [10] or DIRSOL [11]. This facility was commissioned by the European Space Agency (ESA) and installed in the Microgravity Science Glovebox (MSG) onboard the International Space Station (ISS). We report here on a series of preparatory experiments performed in lab-conditions at ACCESS e.V. and at the E-USOC Centre in Madrid using two distinct, but analogous engineering models of the Transparent Alloys Facility. Microgravity experiments were successfully performed in early 2020 and will be reported in a dedicated publication.

2. Experimental

The experimental alloys succinonitrile–(23.6±0.2)(D)camphor (SCN-DC) [1, 12] and succinonitrile–(24.2±0.1)(D)camphor–(0.47±0.03) neopentyl glycol (SCN-DC-NPG) [2] (all in wt.%) were prepared inside a glove-box under Ar using a 300 ml hermetic glass vessel in amounts of 78.5 and 40.4 g, respectively. The vessel was equipped with a specific interface to fill experiment cuvettes. The procedure of alloy preparation was as follows: the purified organic substances were weighted on a digital balance with a precision of ±1 mg and filled into the vessel with the amount required to achieve the desired alloy composition. The purification and characterization of the pure substances was the same as previously described in [1, 2]. In order to remove absorbed gases the pressure in the vessel was reduced by applying vacuum for a duration of 15-20 s, after which the vessel was hermetically closed. The vessel was then heated up to 80 °C to

melt/dissolve the substances and obtain a homogeneous liquid and to fill the transport syringe. Two types of cuvettes, supplied by Hellma® Analytics [13], were manufactured from optically polished quartz glass with 2 mm thick walls and inner dimensions 1mm x 20mm x 200 mm (4 ml total volume, Type 1) and 1mm x 6mm x 100 mm (0.6 ml total volume, Type 2). Filling was equally done inside the glove-box by transferring the liquid alloy from the vessel into the preheated cuvette, followed by hermetic closing of the cuvette. The cuvettes Type 1 were designed for growth experiments in a lab facility (BTA). Cuvettes Type 2 were used in the "Transparent Alloys" facility (STA), described in detail by Ludwig et al. [10].

The temperatures of hot- and cold-zone for the experiments were maintained at 70.0 and 12.0 °C for the BTA and 65.5 and 10.5 °C for the STA. The temperature gradient (G) used in the first and the second apparatus was determined to be 5.2 and 3.7 °C mm^{-1}, respectively, using thermocouple measurements similar to those described in [3, 4, 14].

The interface recoil (L_{IR}) during solidification, including insignificant thermal field shift while withdrawing, was measured in each experiment based on images captured by a front camera (perpendicular to the cuvette movement) with a 360 s time interval. Withdrawal of the sample cuvette from the hot to the cold zone was performed by means of high-resolution linear actuators. The true growth velocity was evaluated based on the recorded withdrawal position L and the interface recoil (L_{IR}), both at time (t), as:

$$V(t) = \frac{d[L(t) - L_{IR}(t)]}{dt}.$$

Within the scope of this study, low withdrawal velocities in the range of 10 to 80 nm s^{-1} were applied to obtain relatively large microstructural features.

The growing eutectic microstructures were digitally recorded frame by frame with a 360 s time span by an oblique-view camera fixed at a 43.6° angle between the optical axis

and the longitudinal axis (withdrawal direction) of the cuvette. The rescaling factor and optical magnification were established through calibration using a special grid inserted in the cuvette perpendicular to its longitudinal axis and filled with experimental liquid alloys. Each acquired frame of 2448 x 2050 pixels covered a sample area of 1.2 mm x 1.0[2] mm for the BTA and 2.4 mm x 1.0[2] mm for the STA facility (Fig. 1*a*). Unfortunately, in oblique view only approximately 1/3 of the microstructure has an acceptably sharp focus (Fig. 1*b*). Therefore, the microstructure characterization was carried out in all cases over a 640 µm x 320 µm region of interest with sharp focus and as few grain boundaries as possible. All area-dependent parameters were normalized to 1 mm^2. The spacing for the eutectic structures, position and number of nearest neighbours were evaluated using the Image Processing Toolbox of MATLAB [15], specifically the "Delaunay triangulation" and "Voronoi diagram" tools. As an example, small regions of rod-like eutectic patterns obtained at steady state growth velocities of 80, 40 and 10 nm s^{-1} are presented in Fig. 2 along with the calculated Voronoi diagrams. For each pattern the distribution of the measured spacing between neighbouring rods is also plotted in Fig. 2. The dependency of the average spacing on growth velocity is shown in Fig. 3 along with the Jackson-Hunt scaling law (dashed line) and its amendment for low velocities following [16] (solid line).

For characterisation of the hexagonal ordering of rods, we have used an order parameter (S_o) introduced by Ratke and Alkemper [7] as

$$S_o = \frac{\sum_i |6-i|\, H_i}{\sum_i H_i}.$$

Here H_i is the frequency with which i-neighbours occur. A perfect hexagonal arrangement gives $S_o = 0$, while a random distribution of rods leads to $S_o = 1$ [7].

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[2] Sample thickness.

For selection of an optimal bin size (*h*) for the plotting and comparison of histograms, the Freedman–Diaconis rule [17]

$$h = 2\frac{IQR(x)}{n^{1/3}}$$

was used, which is based on the interquartile range (*IQR*) and number of observation (*n*) in the sample x. The resulting histograms in the present work are presented as kernel density estimate plots (kernel smooth histograms) [18, 19].

In a first experimental series steady state growth was obtained at velocities 80 nm s^{-1}, 40 nm s^{-1} and 10 nm s^{-1}, respectively during extended growth times of 15 hours for each velocity (Fig. 4*a*).

Furthermore, transient experiments with distinct velocity-time profiles and incremental velocity changes were performed at three different velocity increments ΔV of 10, 3.5 and 0.17 nm s^{-1}. For the smallest increment value of 0.17 nm s^{-1} quasi-continuous deceleration / acceleration conditions were obtained. Examples of the programed and evaluated *V-t* profiles are presented in Figs. 4*b* to *f*. The bold line represents the applied pulling velocity, while thin line with points represents the true growth velocity taking into account the interface recoil.

The following profiles were applied:

(i) The V-type profiles (Figs. 4 *b*, *c* and *e*) comprised a stepwise decrease of the withdrawal velocity from 80 to 10 nm s^{-1}, and after a constant velocity plateau a stepwise increase back to 80 nm s^{-1}, using different velocity increments. This resulted in different but constant values of deceleration ($a<0$) or acceleration ($a > 0$) in the range of $|a|$ from 0.8 to 13 pm s^{-2}.

(ii) The U-type profiles (Figs. 4 *d* and *f*) involved an exponential decay of the velocity by a function $V = 7 + 73e^{-(t-t_s)/C}$ followed by an exponential increase $V = 7 + 3e^{(t-t_s)/C}$ in the same velocity range as above, i.e. from 80 to 10 nm s^{-1} and from 10 to 80 nm s^{-1}, respectively. Here *C* is so-called time constant, *t* is the actual time and t_s is the time at which the deceleration or acceleration starts (all in seconds). For each individual profile the constant *C* was selected from the range 4320 s to 43200 s that resulted for this series of experiments variation of local |*a*| value at attaining of reference velocity *V* = 40 nm s^{-1} in the range from 0.7 to 7 pm s^{-2}. These profiles were designed to mimic a Jackson-Hunt type scaling at each stepwise change of velocity (see, for example, bold zigzag line in Fig. 4*d*).

(iii) The RV-profile (see Fig. 4*e*) and RU-profile (see Fig. 4*f*) are reversed V- and U-type profiles, respectively, which start with the acceleration phase.

All profiles types were run using different acceleration / deceleration parameters, as listed in Tables 1.1 through 2.3. A total of 27 experiments were performed, among them 16 experiments with V-type profiles, 9 experiments with U-type profiles, 1 experiment with reversed V- profile and one with reversed U-profile, respectively. The major part of the experiments were performed with alloy SCN-23.6DC. Three experiments were performed with alloy SCN-24.2DC-0.5NPG. When performing the experiment series, the sample was re-melted after each experimental run and equilibrated in liquid state at least for 24 h before starting the next experiment. For all transient experiments the duration of initial unidirectional solidification stage with velocity of 10 or 80 nm s^{-1} was always long enough to ensure that the average spacing falls inside the range of 24.0±2.2 μm and 11.0 ±1.0 μm, respectively. These ranges are typical error bars from repeated steady state experiment (see Fig. 3).

3. Experimental results and discussion

This section describes the results of the *in-situ* observation of rod-like patterns in the SCN-23.6 DC (wt. %) alloy during transient solidification experiments with distinct velocity-time profiles (compare Fig. 4) with respect to the spacing evolution and the evolution of the hexagonal order parameter. We present the evolution of the rod-like eutectic patterns obtained in different transient experiments for all profile types (V, U, RV and RU), while focussing mainly on those which have been performed with the smallest velocity increment ΔV = 0.17 nm s^{-1}. The analysis results are reported as follows:

(i) First, we analyse the spacing distribution for a selected instant in time, $t|_{V=40}$, when the growth velocity along the distinct transient profiles reaches V = 40 nm s^{-1} and compare it to the reference steady state distribution obtained at constant growth velocity V = cst.= 40 nm s^{-1}. This analysis is described for the experiments performed with the smallest velocity increment ΔV = 0.17 nm s^{-1} and average $|a|$ = 2.1±0.3 pm s^{-2} (experiments no. 14 in Table 1.1 and no. 5 in Table 2.1).

(ii) Secondly, we analyse and discuss the spacing evolution during the entire experiment time for two V-type experiments, performed at $|a|$ = 3.3±0.1 pm s^{-2} and $|a|$ = 5.0±0.2 pm s^{-2}, respectively. We follow the evolution of the rod spacing and the order parameter S_0 during all stages of the experiments. We further present the mechanisms of spacing adjustment found to operate during deceleration and acceleration. This analysis is described for the V-type experiments performed with the largest velocity increment ΔV = 10 nm s^{-1}.

(iii) We summarize the observations gained from all profile types (V, U, RV and RU) and applied conditions (ΔV and $|a|$) with respect to the spacing distribution and the order parameter established when reaching the growth velocity V = 40 nm s^{-1}.

Fig. 5 and Fig. 6. display the spacing distribution established upon attaining the growth V = 40 nm s^{-1} along the transient V, RV, U and RU-profiles for the case of deceleration from 80 → 10 nm s^{-1} (Fig. 5) and acceleration from 10 → 80 nm s^{-1} (Fig. 6), respectively. The figures show the histograms of the measured spacing distribution as well as micrograph snapshots with superposed Voronoi diagrams. The reference histogram and micrograph snapshot for the stationary growth with V = 40 nm s^{-1} are displayed for comparison (compare also Fig. 2*c* and 2*d*). It is noteworthy to observe from Fig. 5 that all transient experiments under decelerating conditions lead to a pronounced shift of the spacing distributions to lower values compared to the steady state reference, while the transient experiments themselves are comparable among one another. This hints to a strong delay in pattern adjustment, i.e. the spacing remains small despite the decreasing growth velocity. From Fig. 6 one can observe that the transient experiments under accelerating conditions also result in a shift to lower spacing values compared to the steady state reference, however the shift is much less pronounced. This observation is counter-intuitive: from delay arguments one would expect to see higher spacing values compared to the steady state reference.

To better understand the above „snapshot“ results taken at the defined time instant $t|_{V=40}$, we analyzed the dynamic response of the rod-like pattern to the imposed transient growth conditions for two complete V-type profiles, corresponding to the experiments no. 2 and no. 3 (compare Table 1.1). These experiments were performed with a velocity increment of ΔV = 10 nm s^{-1} at $|a|$ = 3.3 pm s^{-2} and $|a|$ = 5.0 pm s^{-2}, respectively. From

these experiments encompassing durations of 19 hours (no. 2) and 16.25 hours (no.3), respectively, we extracted 22 or 23 images and followed the evolution of the rod patterns in a region of interest 640x320 µm over time. Smaller images (570x170 µm) from the analysed regions are provided as supplementary material. The analysis results are shown in Fig. 7*a* through 7*c* for experiment no. 2 and in Fig. 7*d* through 7*f* for experiment no. 3. The presented plots are as follows:

The diagrams in Fig. 7*a* and Fig. 7*d* display the evolution of the mode value of the spacing λ_{hm} as function of time given with hollow symbols connected by a solid line. The dotted line represents the evolution of the spacing which would be expected if the transient pattern would continuously adjust to reach steady state values without delay. The full symbols with error bars show the experimentally measured steady state values of λ_{hm} obtained for V = 10, 40 and 80 nm s^{-1}. The diagrams show the delayed response of the patterns to the imposed transients and steep "events" related to specific spacing adjustment processes. Events marked "A" on the deceleration path correspond to an adjustment process which involves a transition from fibrous to vermicular structures, followed by a slow recovery of the fibrous morphology (see Fig. 8 and Fig. 9). Events marked "B" on the acceleration path correspond to rod splitting (see Fig. 8 and Fig. 9). Furthermore, two characteristic values are marked in Fig. 7*a* as Δ_1 and Δ_2 and in Fig. 7*d* as Δ_3 and Δ_4, indicating the difference between the transient and the steady state value of λ_{hm} at the time instant when the growth velocity reaches V = 40 nm s^{-1}. Altogether, the data lead to the following conclusions:

Upon decelerated growth the increase of the eutectic spacing is slow, likely being limited to rod elimination events at domain boundaries only. Accordingly, the pattern grows in a state with overly small spacings. At the onset of event "A" the ratio R between the

measured spacing λ_{hm} and the steady state spacing λ_{ss} reaches R = 0.577 in experiment no. 2 and R = 0.68 in experiment no. 3. We recall Fig. 3 to emphasize that the steady state spacing λ_{ss} includes the amendment to the Jackson-Hunt scaling law as proposed by Akamatsu et al. [16] to account for the overstability of small spacings. After event “A” and the reorganization of the rod-like pattern the spacing never reaches steady state values, despite the fact that the growth velocity remains constant over a long period of time. The system thus enters the acceleration phase of the experiment without having established a stable steady state pattern.

Upon acceleration the pattern responds with only a small delay to the imposed transient with a rod splitting event labelled “B”. Rod splitting is seen to produce smaller spacings than expected (compare Δ_2 and Δ_4) which slowly evolve to reach the steady state values towards the end of the experiment.

The highly dynamic evolution and specifically the disruptive reorganization events “A” and “B” impact on the degree of order, as shown in Fig. 7*b* and 7*e*. The order parameter S_0 increases during the experiments and especially during the events “A” and “B”.

Finally, we propose a convenient and instructive plot of the obtained results not as function of time, but as function of the growth velocity which is the true growth velocity evaluated from the experimental data recorded by the side view camera. These plots are presented in Fig. 7*c* and 7*f*, respectively. They show the hysteresis loop of λ_{hm}–V generated in response to the imposed transients. As before, the dotted line shows the steady state behaviour λ_{ss}–V (compare Fig. 3). These plots are instructive because they clearly show the pronounced delay of pattern adjustment during the deceleration phase and the comparatively faster response during the acceleration phase, however both

entraining sharp reorganization events. When comparing Fig. 7*c* with Fig. 7*f* one is tempted to conclude that the higher acceleration / deceleration imposed in experiment no. 3 (Fig. 7*f*) leads to narrowing the hysteresis loop. We shall show in a forthcoming publication that this is not the case, at contrary, the hysteresis loop widens as $|a|$ increases. The narrower hysteresis loop observed for experiment no. 3 compared to experiment no. 2 most likely results from structural defects like domain boundaries and grain boundaries. Thus, the presence of a thermal groove at the grain boundary, i.e. hyperbolic curvature, as well as surface energy anisotropy, which forces the grain boundary to be driven to replace the high surface energy grain with grain of lower surface energy, induces a drift of the pattern. This motion, like in case of artificial transverse temperature gradient, facilitates the pattern reorganization leading to rapid generation of a regular array of lamellae/rods [20]. Therefore increase of density of such defects could result in narrower width of the loop *via* intensification of early stage adjustments. Unfortunately, it was unfeasible to compare grain boundary networks in our samples since only small parts from complete solid-liquid interfaces were monitored (see Section 2). Other biases may arise from convective fluid flows in the thick-wall cartridge, since these experiments are conducted under Earth gravity conditions.

The snapshot images and the corresponding Voronoi diagrams in Fig. 8 and Fig. 9 illustrate the patterns with focus on the abrupt transitions during the events “A” and “B”. The full set of images and tabulated data are provided as supplementary material for both experiments.

In an attempt to compile all experiments, we plotted the minimum (λ_-), maximum (λ_+) and mode value (λ_{hm}) of the spacing distributions evaluated for the time instant $t|_{V=40}$ as function of the acceleration / deceleration, i.e. measured when reaching the growth

velocity of 40 nm s^{-1}. For U-type and RU-type experiments, where $|a|$ is not constant, we equally chose for $|a|$ the value upon reaching the growth velocity of 40 nm s^{-1}. For $|a| = 0$ we included the steady state values obtained at V = cst.= 40 nm s^{-1}. For reference the plot also includes the reference spacing values from the steady state experiments at V=10 and 80 nm s^{-1} as filled circles. The results are presented in Fig.10. For the sake of clarity we grouped the V-type experiments with high velocity increment in Fig. 10*a*, the V-type and RV-type experiments with small velocity increment in Fig. 10*b* and U-type as well as RU-type experiments with small velocity increment in Fig. 10*c*. To guide the eye, we connected the experiment data-points with a trend-line, letting yet unknown "scatter" to clearly appear in the trend. The selection of the time instant $t|_{V=40}$ is somewhat arbitrary and only due to the fact that steady state reference experiments were available for V = 40 nm s^{-1}. The plots presented in Fig. 10 would look different at other time instants. Nonetheless, it shows that if the magnitude of $|a|$ is high, e.g. $|a|$=13 pm s^{-2}, the dynamically attained spacings $(\lambda_-, \lambda_+, \lambda_{hm})|_{V=40}$ differ largely from the reference steady state spacings at V=40 nm s^{-1}, which are represented by dotted horizontal lines. In fact, it can be seen that for $|a|$=13 pm s^{-2} the measured spacings remain close to the steady state spacings at V=80 or V=10 nm s^{-1}, i.e. the initial spacings. As the magnitude of $|a|$ decreases, the dynamically attained spacings $(\lambda_-, \lambda_+, \lambda_{hm})|_{V=40}$, gradually approach the reference steady state spacing. We expected a monotonic increasing behavior of the function $\lambda=f(a)$ for deceleration and a monotonic decreasing behavior for the acceleration, with the two branches merging at the steady state reference for a=0. However, the experimental data for $|a|$= 3.3 pm s^{-2} and $|a|$= 5.0 pm s^{-2} deviate significantly from the monotonic trend being local extrema marked Δ_1 and Δ_2 in Fig. 10*a* and Δ_3 and Δ_4 in Fig. 10*d*. They correspond to the spacing off-sets shown in Figs. 7*a, d* and 7*c, f*. From Figs.

7*c, f* it is straight forward to see that the captured system state is outside the hysteresis loop. Outside the hysteresis loop the system's state will sensitively depend on local defects (rod merging / Event A) and on stochastic structural reorganizations (rod splitting / Event B).

Finally Fig. 11 displays the dependency of the order parameter S_0 on the acceleration / deceleration measured upon reaching the growth velocity of 40 nm s^{-1}. All experiments are combined in this diagram including, for $|a|=0$, the steady state reference values from 4 independent measurements being in a range of 0.40-0.49. The diagram shows that for the time instant $t|_{V=40}$ virtually all analyzed patterns are more disordered than the steady state reference patterns with the disorder being more pronounced on the acceleration side compared to the deceleration side. The last could also be perceived *via* comparison series of patterns presented in Figs. 5 and 6.

Taken together, the results are in contradiction with the results from Allkemper and Ratke [7], who observed an increasing degree of order under accelerated growth conditions. Furthermore, we observe the coexistence of fibrous and vermicular structures only in decelerating growth conditions, specifically during event "A", while Kellner et al. [8] observed the coexistence for accelerating growth. Further detailed analysis is required to better comprehend the behaviour of eutectic growth under imposed velocity transients.

4. Conclusions

In this work we reported ground-reference results from a series of transient solidification experiments with the organic eutectic alloys SCN-23.6 DC (wt.%) and SCN-24.2DC-0.5NPG (wt.%), which have been performed in preparation of microgravity

experiments using a new multi-user facility called Transparent Alloys (TA) [10] or DIRSOL [11]. In 1g lab conditions we investigated the response of rod-like eutectic patterns to imposed transients, involving defined acceleration and deceleration of the growth velocity. The patterns have been recorded in-situ in oblique view and were analysed for a region of interest of 640 μm x 320 μm over long periods of time. The time dependent growth velocity and the associated acceleration / deceleration were determined using images from a side-view camera.

The results presented here, mainly refer to the spacing distribution and the hexagonal order parameter S_0, dynamically attained at a defined time instant, e.g. at the moment when the local growth velocity reaches V = 40 nm s^{-1} along deceleration 80 → 10 nm s^{-1} or acceleration 10 → 80 nm s^{-1} paths. The major result from this analysis is that the order parameter S_0 is increasing, meaning that the hexagonal order is deteriorating under transient growth conditions compared to steady state conditions. We could not observe an increase of order for either imposed acceleration or deceleration, mainly because spacing adjustment is accomplished by abrupt morphological transitions which destroy the previous order.

The abrupt morphological transitions are clearly identified as sharp events along an experiment cycle 80 → 10 → 80 nm s^{-1} and could conveniently be seen in hysteresis loop diagrams. Upon deceleration the abrupt spacing adjustment event corresponds to a transition from fibrous to vermicular morphology. Upon acceleration the abrupt spacing adjustment event corresponds to rod splitting. Hysteresis loop diagrams are a convenient way to capture the dynamics of the system and shall be further employed for a full analysis of experimental data obtained in microgravity onboard the ISS.

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Electronic supplementary material

The online version of this article contains supplementary material, which is available to authorized users.

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