In-situ and real-time investigation of the columnar-equiaxed transition in the transparent alloy system neopentylglycol-camphor onboard the sounding rocket TEXUS-47

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Abstract. The low-gravity experiment TRACE (TRansparent Aloys in Columnar Equiaxed solidification) has been performed onboard the sounding rocket TEXUS-47 to enable the investigation of dendritic growth and the dendrites’ columnar to equiaxed transition during solidification. Low-gravity conditions provide solidification under diffusive heat and mass transfer conditions and without sedimentation or buoyancy of equiaxed dendrites or nucleation seeds to simplify the boundary conditions for dendritic microstructure simulation. In addition the transparent organic alloy system Neopentylglycol (NPG) - (D)Camphor (DC) was used to allow for a real-time and in-situ observation of the microstructure evolution with standard optics. For the flight experiment all relevant experimental parameters like thermal gradient, solidification velocity and undercooling within the bulk liquid and at the columnar dendritic tips have been determined by image analysis or from thermocouple recordings within the solidifying alloy. This allows a very detailed comparison with results of existing models for dendritic growth and for columnar-to-equiaxed transition. Here we present a summary of the experimental findings in comparison with results of some of the theoretical models.

1. Introduction
Dendritic microstructures are common to a large variety of solidification processes in technical applications. Dendrites may be subject to coarsening or phase-transformations towards their final microstructure at ambient, but the mechanical properties are often linked to the primary grain formation from the liquid phase. The grain structure of the primary alloy phase results from a competition of growth and nucleation, depending on the solidification conditions and properties of the alloy. The columnar-to equiaxed transition (CET) in grain grown of as-solidified alloys is identified as a change in microstructural features, like grain size and form and can lead to mechanical inhomogenities. As a simplified rule-of-thumb columnar dendritic growth is obtained at high thermal gradients and low cooling rates at the interface between solid dendrites and liquid melt and equiaxed dendritic growth vice versa. The columnar grains are oriented and elongated, while equiaxed grains have more isotropic properties and are formed upon nucleation and growth. As a consequence, equiaxed grains have generally smaller grain sizes with more spherical shapes and random crystallographic orientations. The CET is in general not favoured for a technical product, since microstructural heterogeneities can lead to mechanical ones. Physical mechanisms and conditions for the occurrence of CET are summarized in [1].
This article focuses on experimental results and a comparison to models of the microgravity experiment TRACE ((TRansparent Alloys in Columnar Equiaxed solidification). In the experiment the low-gravity environment of the sounding-rocket TEXUS-47 has been used to provide convection- and sedimentation/buoyancy-free solidification processing. A transparent organic alloy Neopentylglycol-Camphor has been used to observe in-situ and real-time the columnar dendritic growth of NPG-dendrites and their CET. This allows the determination of parameters like solidification velocity and dendrite tip undercooling or nucleation undercooling for equiaxed growth. We compare the experimental results with existing models for dendritic growth [2-5] and CET [6], the later with different approximations.

2. Experimental set-up

The experimental set-up, procedure, boundary-conditions and first results have been summarized in [7]. Here, we recall the main features and results. The materials NPG and DC have been purified, alloyed as NPG-37.5wt.-%DC and filled into the transparent experimental cell. The experimental volume in the cell is 20 mm width x 16 mm height x 1 mm thickness. The experiment is controlled by the temperatures at the bottom and the top of the experimental cell, defining the melting and solidification direction within the cell. Observation is carried out perpendicular to the height and width-axes. Macro-images of the size of the cell are acquired, as well as detail images, with two different CCD-cameras, field-of-views and optical resolutions. The columnar growth was started on ground before lift-off of the sounding rocket with a low solidification speed, corresponding to a cooling-rate of -0.2 Kmin^{-1}. Within the low-gravity period of 410 s onboard the sounding rocket TEXUS-47 a gravity level lower than ±4 mg in all directions was obtained. The low-gravity period is within +60 s and +470 s after lift-off, the initiation of CET was started by setting the cooling-rate to 2.0 Kmin^{-1} simultaneously to the beginning of the low-gravity period at t=+60 s. Temperatures were measured within the bulk material by five thermocouples of diameter 0.25 mm, that were inserted through one side of the cell. From the macro-images and the thermocouple recordings the position, velocity and temperature of the dendritic interface were measured in columnar growth. After nucleation of equiaxed dendrites their density and volume fraction were determined as a function of time. The temperature gradient determined from the thermocouple recordings.

3. Experimental results

3.1 CET parameters

For comparison with CET-models the critical parameters at the CET have been determined from the experiment [7] and are summarized in table 1.

| Parameter                  | Value         | Comment                                      |
|----------------------------|---------------|----------------------------------------------|
| Time                       | 435 s         | After lift-off                               |
| Front undercooling         | 11.5±1 K      | Averaged along front [7].                    |
| Front velocity             | 13.5±0.5 µms^{-1} |                                            |
| Equiaxed volume fraction   | 0.36          |                                              |
| Thermal gradient           | 16.5±1 Kcm^{-1} | Along solidification direction [7]          |
| Equiaxed grain density     | 0.5 mm^{-3}   |                                              |

In addition to these critical parameters the distribution of nucleation temperatures are determined here, as well as the relationship between undercooling and solidification velocity.
3.2 Nucleation temperatures

In figure 1a we see the macro-image obtained at the CET at \( t = 435 \) s after lift-off, in which equiaxed dendrites are present ahead and engulfed in the columnar dendritic front. The equiaxed dendrites are of different sizes and at different axial positions; their volume fraction is 0.36 \[7\]. We have determined the position of the equiaxed dendrites from the macro-images at smallest visible size. With an optical resolution in the focal plane of about 30 µm, that size is about 50 µm. With the assumption of a constant axial temperature gradient in between two thermocouples, the temperature at the position of these small equiaxed dendrites was determined from the thermocouple recordings above and below that position at the time of occurrence and by linear interpolation. In fact, we assume that their temperature is the same as the nucleation temperature and that release of latent heat or curvature effects during growth towards the small size do not effect the determination of the temperature. Figure 1b shows the frequency distribution of the nucleation undercooling for all 26 equiaxed dendrites within the experiment obtained by the procedure described above.

The nucleation undercooling is calculated relative to the experimentally determined liquidus-temperature of \( T_L = 64\pm1^\circ\text{C} \) \[7\]. A distribution between 8.5 and 12.0 K is found and not a single value for the nucleation temperature. The average and standard deviation of the distribution are given as 10.3±0.9 K. During the experiment a tendency towards higher nucleation temperatures was observed.

The evolution of equiaxed grain temperature from nucleation towards engulfment in the columnar front is shown in figure 2 in comparison to the columnar front temperature. The undercooling of the equiaxed dendrites was determined at their centers. The columnar front undercooling is increased from its steady-state value of about 7 K at \(-0.2\) Kmin\(^{-1}\) to about 11.7 K at the end of the microgravity period upon changing the cooling-rate. The “hump” from \( t = -100 \) s to +100 s corresponds to a technical mal operation and not to a physical effect. The equiaxed dendrites nucleate ahead of the columnar front at lower temperatures. Four equiaxed dendrites have been analyzed (see figure 3) from detail-images and show nucleation temperatures at the lower limit of the nucleation temperature frequency distribution (8.3-9.0 K). Small differences in the temperature determination exist between the analysis from the macro-image (figure 1) and the detail-images (figure 3) due to the higher resolution in the latter. This leads to earlier recognition of equiaxed dendrites in the detail images at lower times (293 s compared to 315 s) and lower nucleation temperatures (8.3 K compared to 8.5 K).

As the equiaxed grains increase in size, their centers move towards the growing columnar front. Thus, the undercooling of the equiaxed dendrites approach the columnar front undercooling. In some
cases the undercooling of the equiaxed dendrites exceeds that of the columnar front. This is related to
the slightly different temperature determination procedures.

![Graph showing undercooling-velocity relationship](image)

**Figure 2:** Evolution of the undercooling of the columnar front and of some equiaxed
dendrites.

### 3.3 Undercooling-velocity relationships

For a comparison to existing theories on dendritic growth for alloy solidification the relationship
between undercooling and solidification velocity was determined from the experiment. This was done
both for columnar and equiaxed dendritic growth. In columnar dendritic growth the parameters were
determined from the macro-images at the applied cooling rates of -0.2 Kmin$^{-1}$ until the first observed
equiaxed grains at -2.0 Kmin$^{-1}$ ($t=315$ s).

The growth of equiaxed dendrites was followed in the detailed images with higher optical
resolution of about 3 µm and at a field-of-view of 2.1 mm in width and 1.7 mm in height. Figure 3
shows a sequence of images with individual equiaxed dendrites growing in time. The undercooling
was calculated by determining the positions of the centre of each equiaxed dendrite and interpolating
their temperatures from the surrounding thermocouples. The result is shown as function of time in
figure 2. The growth rate was calculated from the change of the equiaxed dendrite size in time. The
size was determined by fitting an ellipse around the circumference of each equiaxed dendrite and by
calculating the average length of the ellipse axes.

Figure 4 shows the result for the columnar front and the four equiaxed dendrites shown in figure 3,
as individual data points. In addition x-error bars are added to the latter to capture the systematic error
by determining the undercooling of the dendrites’ centre and not their tips.
Figure 3. Nucleation and growth of equiaxed dendrites ahead of the columnar dendritic front. Each image of size 6.6 x 2.9 mm² consists of 8 individual images. The time to take the images by shifting the camera position is roughly 14 s. The images correspond to (top) \( t = 293.0 \) s – 307.3 s; (centre) \( t = 331.0 \) s – 345.2 s and (bottom) \( t = 368.0 \) s – 382.2 s.
4. Theoretical models

4.1 Undercooling-solidification velocity relationships

The models from Burden-Hunt (BH) [2], Lu-Hunt (LH) [3] and LGK/KGT [4,5] have been plotted in figure 5a in addition to the experimental data. As can be seen, none of them is able to describe the experimental data correctly. Within the LGK/KGT-theory a stability parameter $\sigma^*$ is used, which is defined as $\sigma^* = 1/4\pi^2 = 0.0253$. In literature deviations from these value for other transparent model alloys are reported, for example $\sigma^* = 0.0192-0.313$ for succinonitrile-acetone [8] or $\sigma^* = 0.081 \pm 0.02$ for NBr$_4$-water [9]. Therefore we decided to perform a fit of the LGK/KGT-theory to the experimental data with $\sigma^*$ as fit parameter. The result is shown in figure 5b with the stability constant obtained as $\sigma^* = 0.007$ for the NPG-37.5wt.-%DC alloy system. In addition a power-law ($V = A^*\Delta T^P$) is fitted to the experimental data, giving an even better fit result. Nevertheless the power-law lacks of theoretical basis. For the power-law fit-values of $A = 2.1 \times 10^{-10}$ ms$^{-1}$ and $P = 4.43$ are found.
4.2 CET-model

Hunt’s model [6] is based on the assumptions of steady-state growth conditions, constant alloy properties, a linearized phase diagram, diffusive transport of mass in the liquid and a constant thermal gradient without release of latent heat during solidification. The same kinetic law (undercooling-solidification velocity relationship, sec. 4.1) is employed for both columnar and equiaxed dendritic growth, while direct interaction between the dendrites is neglected. The existence of several dendrites is accounted for in an extended volume formulation. Heterogeneous nucleation at a given nucleation density with a single value for the critical nucleation undercooling is assumed. The CET-criterion is based on the equiaxed volume fraction $\phi_E$, which is calculated in the model. For fractions $\phi_E > 0.49$ equiaxed growth is assumed to dominate columnar growth.

The original model [6] was developed further by several authors to account for heat transport and the release of latent heat [6, appendix], LGK/KGT-kinetic law [10] and non-standard stability constants $\sigma^*$ [11], non-equilibrium effects in thermodynamics [12] and a Gaussian distribution of nucleation undercooling [10, 13]. The general assumption of $\phi_E = 0.49$, known as the “mechanical blocking”-criterion was discussed critically [14], while other authors take into account solutal [15] or thermal [16] interactions of the dendrites.

Here we calculate the predictions based on the original model [6], taking into account the known thermophysical properties [7] of the alloy and LGK/KGT kinetic-law [4,5] with the original as well as the best-fit stability constant in the latter. Furthermore we investigate the effect of nucleation density $N_0$ and critical growth velocity $V$ and compare the predictions for a single value of the single nucleation undercooling (at the average value of $\Delta T_N = 10.3$ K) with the assumption of a Gaussian distribution fitted to the experimental distribution (figure 1b). The results for $\phi_E$ are summarized in table 2, together with the experimental result from TRACE.

**Table 2.** Results of the model predictions following [6], in comparison to experimental results.

| Kinetic law | $\sigma^*$ | $N_0 / [m^3]$ | $\Delta T_N / [K]$ | $V / [\mu m s^{-1}]$ | $\phi_E$ | Comment |
|-------------|------------|---------------|---------------------|---------------------|---------|---------|
| (1) LGK/KGT | 0.0253     | $5 \times 10^8$ | 10.3                | 13.5                | 0       | (columnar) standard |
| (2) LGK/KGT | 0.007      | $5 \times 10^8$ | 10.3                | 13.5                | 0.997   | (equiaxed) Best-fit $\sigma^*$ |

![Figure 5a](figure_4). Comparison of experimental data with theoretical models.

![Figure 5b](figure_4). Comparison of experimental data with theoretical models and power-law fit.
As can be seen from table 2, the Hunt model in combination with LGK/KGT kinetic law results in prediction of grain growth, which is either almost completely columnar (\( \phi_E \approx 0 \)) or equiaxed (\( \phi_E \approx 1 \)). This holds for the standard stability constant \( \sigma^* = 0.0253 \) (1) and the calculation with the best-fit value of \( \sigma^* = 0.007 \) (2). Assuming a reduced nucleation efficiency of 1% (100 times higher seed density) (3) or a lower solidification velocity at CET (from \( t = 420 \text{s} \)) (4) do not improve the predictions.

With the power-law fit the difference between experimental result (\( \phi_E = 0.36 \)) and the standard calculation is slightly decreased, while using a gaussian distribution for the nucleation temperatures does not improve. The good agreement for parameters given in (6) with the experimental result is misleading, since a critical velocity of 11.0 \( \mu \text{m s}^{-1} \) corresponds to \( t = 420 \text{s} \), at which the experimental equiaxed volume fraction was determined to be \( \phi_E = 0.17 \). This is again significantly smaller than the model result \( \phi_E = 0.39 \).

### 5. Conclusions

Results of the low-gravity experiment TRACE performed onboard the sounding rocket TEXUS-47 are summarized here, in addition to previously reported data [7].

The nucleation temperature distribution was determined, showing values between 8.5 and 12.0 K with an average and standard-deviation of 10.3±0.9 K. The distribution is related to heterogeneous nucleation on substrates of different size or type.

The undercooling-solidification velocity relationship is similar for the columnar front and equiaxed dendrites growing ahead of the front. Comparison with dendrite growth models from Burden-Hunt [2], Lu-Hunt [3] and the standard LGK/KGT-model [4,5] are not capable to predict the measured relationship correctly. Possible explanations can be the simplified geometries of dendrites in the models.

A fit of the stability constant \( \sigma^* \) within the LGK/KGT-model results in \( \sigma^* = 0.007 \), which is more than three times less than the standard value. This explains why high undercoolings are found at relatively low solidification velocities.

A power-law fit gives the best agreement to experimental results, but lacks of physical background. Nevertheless, it offers the advantage that alloy properties do not have to be known for predictions of CET in the model of Hunt. In contrast, the kinetic laws entering Hunt’s model do depend on alloy properties for LH, BH, LGK/KGT [2-5].

Hunt’s model is used to predict the equiaxed volume fractions at the columnar front. This is the first time that all input parameters for modeling are known and a direct comparison with the experiment is possible. Using the LGK/KGT-kinetics within Hunt’s model results in the predictions of either complete columnar or equiaxed dendritic growth for all variations carried out. The same holds for the power-law-kinetics, which improve the predictions slightly. We conclude that none of the kinetic laws in combination with Hunt’s model for mechanical blocking is able to predict the experimental CET-results quantitatively in terms of the equiaxed volume fraction. Interestingly, the
conditions applied experimentally to obtain columnar growth (−0.2 Kmin⁻¹ corresponding to a steady-state velocity of 2.02 µms⁻¹) and to force the CET in a transient process (−2.0 Kmin⁻¹ corresponding to a steady-state of velocity 20.2 µms⁻¹) result in correct predictions in Hunt’s model.

Consequently, proposals to tackle the disagreement at the CET are: (i) the dendrite shapes should be resolved on the microscopic scale (for example with phase-field-simulations), (ii) solutal interaction should be taken into account and (iii) the CET should be calculated in the transient state.

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