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Investigation of structure formation during freeze-casting from very slow to very fast solidification velocities

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Abstract

The ice-templated structure formation of water based suspensions was investigated from very slow ($< 1\mu\text{m/s}$) up to very fast ($> 100\mu\text{m/s}$) solidification velocities, by analyzing the microstructure development in the frozen as well as in the green state. Maps for the microstructure development were established, showing transitions from a planar to lamellar and lamellar to isotropic microstructure in dependence of particle size, solids content and solidification velocity.

Keywords: freeze-casting, microstructure development

1. Introduction

Freeze-casting is a closely examined processing route for macro porous ceramics in recent years. Subsequently, a lot of efforts were put to this production technique which shows the ability in using a wide variety of materials from nano- to macro-scaled powders and dispersion liquids [1, 2, 3, 4, 5, 6]. A recent review article by Deville [7] gives a good summary of all these methods.

The freeze-casting processing route begins by unidirectional freezing of a liquid suspension (water, camphene and other dispersion liquids). Water is commonly used as solvent and was used for the results presented here. By freezing water based suspensions, ice lamellae are formed, pushing the ceramic particles into the interlamellar spaces [7]. After freeze-drying, a

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porous ceramic preform remains whose pore size and shape is defined by the former ice crystals. Up to now, it is well known that increasing the solidification velocity decreases the spacing of the ice crystals, while increasing the solids content the spacing of the ice crystals increases too [8]. Furthermore, the total porosity is also affected by the solids content of the suspension [9, 10]. The microstructure evolved after sintering can be categorized by different morphologies depending on the solidification velocity [8]. At high velocities, a dense layer of particles is formed, which can be found in the bottom region of the samples where high cooling rates prevail. Slightly decreasing the solidification velocity, a columnar microstructure is formed changing to a lamellar microstructure as the velocity is decreased further more. In earlier publications by Rempel and others [11, 12, 13, 14, 15] the interaction of particles with a moving ice-liquid interface was described theoretically. They found a transition from pushing to trapping of the particles by the planar solidification front with increasing solidification velocities.

The aim of the present work is to evaluate the observed microstructure formations of sintered bodies by experimental investigations on non-sintered bodies over a broad range of cooling rates. By that, the above referred studies can be linked.

For this purpose the microstructure transition regions for water based suspensions from particle size, solids content and solidification velocity was analyzed quantitatively. In order to avoid the influence of sintering artefacts such as shrinkage and potential microstructure corruption, the microstructures were investigated in the frozen as well as in the green state. For the first time the microstructure development was investigated over an extended solidification range of four orders of magnitude beginning with slow ($< 1 \mu\text{m/s}$) up to fast ($> 100 \mu\text{m/s}$) velocities.

2. Experimental

Different water based suspensions were used for the experiments. The characterized powder systems are shown in Table I.

Alumina suspensions were mixed with 0.53 wt.% (CT3000SG), 0.5 wt.% (AA-03) and 0.05 wt.% (AA-3) of dispersant (Dolapix CE 64, Zschimmer & Schwarz GmbH, Germany) in distilled water and ball-milled for about 4 h. Solids content of the suspensions was varied from 5 up to 30 vol.%. Experiments with larger particle sizes were conducted with water based polystyrene suspensions with a solids content of 5 vol.%. Freezing was done in cylindrical acrylic glass molds of different diameters. For the alumina-based suspensions, an inner mold diameter of 30 mm and a height of 45 mm was used, whereas for the polystyrene suspensions the inner diameter was 8 mm and the height 10 mm.

(a) Investigation of planar ice growth:

For investigation of the planar ice growth, very slow solidification velocities had to be realized. For this purpose, the acrylic glass molds were glued on a thin copper plate and placed on a precooled plate of a freeze-dryer (Sublimator 400K, Zirbus Technology, Germany). The top of the glass frame was open so that the upper surface of the mould was exposed to the ambient atmosphere at room temperature. In a first step, pure water was frozen to heights of a few millimetres. Afterwards the plate of the freeze-dryer was adjusted to a temperature of $0.75 \pm 0.25 \text{ }^\circ\text{C}$ and the suspensions were poured on the planar ice front. The ice decreases the heat flow out of the suspensions and avoids supercooling effects, what finally leads to very slow solidification velocities. The microstructure development was investigated in-situ by a Long-Distance-Microscope (K2, ISCO-OPTIC GmbH, Germany).

The solidification velocity of the suspensions was verified with the help of markers at the outer side of the molds (1 mm spacing perpendicular to the freezing direction). Photographs of the solidification front, taken in fixed intervals, allowed a measurement of the freezing process over time.

(b) Investigation of the lamellar ice growth:

Both single-sided as well as double-sided cooling experiments were carried out in the range of solidification velocities necessary for lamellar ice growth. These velocities are above those necessary for planar ice growth. For single-sided cooling experiments, freezing was done on a precooled copper plate placed in a freeze-dryer while the plate temperature was kept constant. The top of the acrylic glass molds were open, so that the upper surface of the suspension was exposed to the ambient atmosphere at room temperature.

For the double-sided cooling experiments, a newly developed double-side cooling setup (DS-setup) was applied (Fig.1), which consists of two copper rods with a diameter of 30 mm whose planar surfaces extend into the cylindrical molds. The temperature of the rods can be changed during freezing, so that constant freezing velocities from 5 up to 30 $\mu\text{m/s}$ could be realized over the total sample height [16].

Single-sided cooling experiments were used as a simple production technique for the in-situ examination of microstructure development over the total sample height. For this purpose, the samples were processed in green state. To stabilize the green microstructure, 10 wt.% of binder (Optapix PAF 60, Zschimmer&Schwarz GmbH, Germany) was added to the suspensions before ball-milling. After freezing, the samples were freeze-dried for about 48 hours. In order to make the samples processable, the green microstructure was infiltrated with resin (Epoxy Resin & Hardener, Buehler GmbH, Germany) under reduced pressure (Cast n'Vac 1000, Buehler GmbH, Germany). For the microstructure characterisation, the samples were cut perpendicular to the solidification direction with a wire saw (Well Diamond Wire Saw, Type 3241, Well Diamantdrahtsägen GmbH, Germany) in plates of 2 mm thickness.

For double-sided cooling experiments, suspensions without binder additives were used and the microstructure was investigated in the frozen state. After freezing, the samples were removed from the acrylic glass molds, subsequently grinded in frozen state to different heights and investigated in the cryostage of a SEM (Leica Stereoscan 440, Leica Cambridge LTD., England). For measurement of solidification velocity in the region of lamellar ice growth, the optically visible solidification front was observed by taking picture sequences with a macro lens.

To realize very fast solidification velocities, small droplets of alumina suspensions were dropped on a pre-cooled copper plate. Cooling was realized with liquid nitrogen at $-196\text{ }^\circ\text{C}$. The average freezing velocity was estimated from the total solidification time and droplet size. The microstructure of the frozen drops was analysed in the Cryo-SEM afterwards.

3 Results

3.1 Investigation of the morphologies during planar ice growth

The freeze-casting process for water-based suspensions has been discussed for solidification velocities above 1 $\mu\text{m/s}$ only [7] and investigations of microstructure development for solidification velocities below this level are lacking. For this purpose, ceramic suspensions were poured on a previously frozen planar ice front (Fig. 2). The suspensions used for these

investigations were alumina suspensions with alumina powder CT3000SG (Table 1). The solids content of the suspensions was varied from 5 up to 30 vol.%. Fig. 2 A shows the progress of solidification over time for a suspension with 5 vol.% solids content and a solidification velocity of 0.06 $\mu\text{m/s}$. The solidification front remains planar, pushing the ceramic particles ahead of the front. Only a few particles are engulfed by the ice, visible as small dark speckles in the image. Increasing the solidification velocity to 1.2 $\mu\text{m/s}$, the planar solidification front becomes instable and a lamellar microstructure is formed, pushing the ceramic particles into the interlamellar spaces. This is visible in Fig. 2 B as dark lines growing from bottom to top.

The transition from planar to a lamellar ice morphology as a function of the solids content of alumina powder was investigated systematically (Fig. 3). The critical transition velocity v_T was determined for each of the suspensions. For 5 vol.% solids content, the transition velocity v_T was about 0.35 $\mu\text{m/s}$. It decreased to about 0.05 $\mu\text{m/s}$ for 30 vol.% solids content. The error bars in Fig. 3 are related to the accuracy of velocity measurements of about 0.02 $\mu\text{m/s}$. The dependence of the transition velocity from the content of alumina powder in the suspension was almost linear within the investigated concentration range. In order to estimate the influence of particle size (see Fig. 10), the transition velocity was determined for a polystyrene suspension with 6.6 μm particle size as well. The transition was at about 0.2 $\mu\text{m/s}$ for a solids content of 5 vol.% polystyrene particles, which is well below the transition velocity obtained for alumina suspensions with the same solids content.

3.2 Investigation of the morphologies during lamellar ice growth

In order to analyse the dependence of lamellae spacing from solidification velocity and solids content, single-sided cooling experiments were carried out. For the analyzation of a wide range of solidification velocities, constant cooling plate temperatures of -10, -20, -30 and -50 $^{\circ}\text{C}$ were chosen. Plate temperature was kept constant within ± 0.25 $^{\circ}\text{C}$. The solids content was varied from 5 to 30 vol.%. The alumina powder used for these investigations was CT3000SG. The results are shown in Fig. 4. The error bars shown in Fig. 4 and Fig. 5 are the standard deviations of the measured lamellae spacing by measuring at least fifty lamellae for each measuring point. For constant plate temperatures, the solidification velocity decreases with increasing distance from the cooling plate over the sample height, resulting in an increasing lamellae spacing [16]. The measurements show, that the empirical dependence of the lamellae spacing λ on the solidification velocity v can be described by a power law ($\lambda \propto v^{-1}$), which is consistent with the results already reported by Deville et al. [8]. Furthermore it is obvious, that the lamellae spacing diverge for experiments at different, but constant, cooling plate temperatures (see Fig. 4). However, the increase of the lamellae spacing over the sample height can not be fully explained by the decreasing solidification velocity alone. This is probably due to lamellae combinations over the sample height during solidification and will be discussed elsewhere.

As the influence of particle size on the lamellae development is not clearly identified in literature yet, experiments at constant solidification velocities were realized with double-sided cooling in the DS-setup (Fig. 5). The major advantage of the double-sided cooling experiments to the single-sided cooling experiments is a nearly constant lamellae spacing over the total sample height. So the lamellae spacing can be determined at different cross section positions which give results that are better statistically secured.

Suspensions with two different median particle sizes of 0.25 and 3.3 μm and solids content of 10 vol.% (see Table I.) were studied. As mentioned above, several cross section positions were evaluated in the region of 5 to 15 mm from the bottom of the sample.

The black curves in Fig. 5 show a shift of lamellae spacing to larger values with increasing median particle size. By increasing the particle size by a factor of 10, approximately a doubling in lamellae spacing was obtained. The grey curve in Fig. 5 corresponds to the experimental data for single-sided cooling as already shown in Fig. 4 (10 vol.%) and compares them to the doubled-sided cooling experiments. As it can be seen in Fig. 5, the dependencies of lamellae spacing on the solidification velocity seems of similar function type.

Solidification velocities realized in the double- or single-sided cooling setups were limited to solidification velocities up to 40 $\mu\text{m/s}$ by the minimum cooling temperatures of the freezing setups of $-50\text{ }^\circ\text{C}$.

To realize solidification velocities well above 40 $\mu\text{m/s}$, small droplets of alumina suspensions (CT3000SG) were placed on a precooled copper plate cooled to $-196\text{ }^\circ\text{C}$. Freezing occurs under such conditions very quickly. For these experiments, suspensions with 10 and 20 vol.% solids content were used. Fig. 6 (A) shows the side view of a fully frozen droplet obtained in the Cryo-SEM. With larger magnification of the area next to the cooling plate (Fig. 6 (B)) the formation of ice lamellae growing from bottom up can be seen. Caused by the high solidification velocities, there is no clear difference in lamellae spacing between the two investigated solids contents. The average lamellae spacing was about 6 to 10 μm for a solidification velocity of 250 $\mu\text{m/s}$ and about 3 μm for solidification velocities of 700 $\mu\text{m/s}$. The solidification velocity was estimated by the total solidification time and the droplet height, measured by image analysis of the SEM picture.

The analysis of the influence of particle size on lamellae spacing is limited to particle sizes of about 3 μm for alumina dispersed in water (Fig. 5). This is caused by fast sedimentation of larger particles. Therefore, experiments with water based polystyrene suspensions were realized. Four different suspensions with a solids content of 10 vol.% and particle sizes of 2.2, 4.1, 6.6 and 15 μm were unidirectionally frozen in the DS-setup at constant freezing velocities in a range from 3 to 20 $\mu\text{m/s}$ and analysed qualitatively. Each symbol in Fig. 7 is representing a single measurement, so no error bars are available. The microstructure formation shows a clear change from lamellar to isotropic above a critical solidification velocity (Fig. 7 B). For a particle size of 4.1 μm , the microstructure is lamellar for solidification velocities of 8 and 10 $\mu\text{m/s}$, but isotropic for 20 $\mu\text{m/s}$. For a particle size of 6.6 μm , the microstructure transition occurs between a solidification velocity of 5 and 8 $\mu\text{m/s}$. Fig. 7 (A) gives an overview of the complete experimental results. It can be seen that the transition velocity from a lamellar microstructure to an isotropic microstructure is shifted to smaller solidification velocities with increasing particle size.

4 Discussion

4.1 Transition of ice crystal morphologies from planar to lamellar and from lamellar to isotropic

The mechanism forming ice lamellae by unidirectionally freezing of water based suspensions was not yet clear. Therefore, the ice morphology was investigated over a wide range of solidification velocities from very slow ($< 1\text{ } \mu\text{m/s}$) up to fast freezing velocities in order to generate a systematic database, which helps to explain the origin of the observed structures.

The experiments with alumina suspensions show, that, starting with a planar solidification front (pure ice), a transition from a planar to a lamellar ice morphology can be observed

(Fig.3). The investigated alumina suspensions underwent this transition for solidification velocities below $0.5 \mu\text{m/s}$, depending on the solids content.

The interaction of particles with a moving planar solidification front was the object of several investigations and showed that there is a transition from pushing to trapping of the particles at a critical solidification velocity v_c [11, 12, 13, 15]. Pötschke and Rogge [14] gave an enhanced model to describe this transition velocity for polystyrene particles. As a function of particle size and temperature gradient at the solidification front, they obtained for the critical solidification velocity v_c :

$$v_c = 3.74 \cdot 10^{-13} \cdot G^{0.5} \cdot R^{-1} \left[\left(\sqrt{m} \cdot m^2 \right) / \left(\sqrt{K} \cdot s \right) \right] \quad (1)$$

G is the temperature gradient ahead of the solidification front and R is the particle radius. Using a reasonable value for the temperature gradient of $G = 1000 \text{ K/m}$, the critical velocity for a particle size of $1 \mu\text{m}$ is calculated to $v_c \approx 30 \mu\text{m/s}$. This value of v_c shows, that the critical velocity for particle trapping is remarkably beyond the measured transition velocity from planar to lamellar ice morphology. Therefore, it can be expected that there is no relationship between these transitions.

For polystyrene particles in distilled water, no transition from planar to lamellar ice morphology was observed by these early studies. Since these studies dealt with highly diluted suspensions, particle-particle interactions in liquid were neglectable and have not to be considered. However, this assumption is not valid for the experiments presented here. This suggests the thesis that the observed transition from planar to a lamellar ice morphology is triggered by particle-particle interactions, i.e. as a result of supercooling effects. It has been shown, that the thermodynamic solidification temperature is affected by particle-particle interactions [17], a comparable effect as the Mullins & Sekerka instability observed in molten metal alloys [7].

Fig. 8 shows a schematical model of this thesis: For very slow freezing velocities, the particles are pushed ahead of the planar ice front for diluted suspensions as well as for concentrated ones. For diluted suspensions, increasing solidification velocities result in an increasing volume fraction of particles which are entrapped by the progressing planar ice front. With increasing solids content, particle-particle interactions are no longer negligible and the concentration profile ahead of the planar ice front leads to constitutional supercooling of the liquid as reported in [18, 17]. This has a destabilising effect on the planar ice front, which finally leads to a lamellar microstructure (Fig. 8).

For alumina suspensions with particle sizes of $0.8 \mu\text{m}$, the lamellar microstructure was maintained up to highest solidification velocities of $700 \mu\text{m/s}$ (Fig. 7). This is no longer the case for increasing particle sizes. Experiments with polystyrene spheres show a transition of microstructure development from lamellar to isotropic as shown in Fig. 7. As already discussed, Eq. (1) gives the critical velocity v_c for trapping of polystyrene spheres by a planar solidification front. Comparing v_c to our experimentally obtained data and, using the temperature gradient at the solidification front of $G = 3000 \text{ K/m}$ as a fitting parameter, a good correlation of v_c with the microstructure transitions can be shown (Fig. 9). With respect to the small suspension molds used for these experiments, a temperature gradient of $G = 1000 \text{ K/m}$ seems to be reasonable whereas $G = 3000 \text{ K/m}$ used for the fitting seems too high. Never the less, this discrepancy seems reasonable regarding further influencing factors in Eq. (1), i.e. the diffusion coefficient of polystyrene spheres in water or the segregation coefficient. These factors could differ to the values assumed by Pötschke and Rogge [14]. For

that reason, it is most likely that the transition from a lamellar microstructure formation to an isotropic one is not caused by a change in ice morphology, but by engulfing the polystyrene particles by the growing ice lamellae. This is schematically shown in Fig. 8 for solidification velocities $v \geq v_c$.

Images of cross-sections from Cryo-SEM support this thesis as they are still showing lamellar overlayer structures for solidification velocities slightly above the critical solidification velocity v_c (see white arrows in Fig. 8).

In this context, microstructure formation can be understood in terms of interacting forces between the solidification front and the particles in the suspension. Without particle-particle interaction forces, the particles are pushed ahead of the growing planar solidification front for slow freezing velocities and are partially engulfed when the velocity increases. This is caused by increasing drag forces on the particles, whereas the disjoining force developed by the interfacial free energy between the particle and the solid phase remains constant [15]. Above the critical solidification velocity v_c , the drag forces are higher than the disjoining forces, leading to complete particle encapsulation. The same mechanisms take place in more concentrated suspensions. Additionally the interaction of the particles with the frozen suspension is superimposed by the formation of ice lamellae well below the critical solidification velocity v_c , triggered by the particle-particle interactions. For velocities below v_c , the majority of the particles are pushed into the interlamellar spaces. Only a small fraction of particles, whose drag forces are higher than the disjoining forces - most likely at the tip of the ice lamellae -, are engulfed. When the growth velocity of ice lamellae is reaching v_c , the ice lamellae can not push the particles into the interlamellar spaces any more, so that the particles have to be engulfed. This finally leads to an isotropic microstructure.

Fig. 10 gives a map of microstructure transitions from planar to lamellar and from lamellar to isotropic, both based on our experimental results shown above. For alumina suspensions with particle size of 0.8 μm , the transition from planar to lamellar ice morphology is shown as black points, which are shifted to higher freezing velocities with decreasing solids content. The dotted line at 5 vol.% solids content shows the prediction for this microstructure transition for increasing particle sizes. This prediction is based on an additional measurement with polystyrene suspension with a particle size of 6.6 μm (see Fig. 3). This can be understood in terms of supercooling effects as discussed above. To reach the critical supercooling necessary for triggering a microstructure transition from planar to lamellar, a sufficient concentration gradient ahead of the planar solidification front is necessary. The particle diffusivity decreases with increasing particle size leading to a sufficient concentration profile at lower freezing velocities.

For higher solidification rates, the ice morphology is building ice lamellae pushing the ceramic particle into the interlamellar spaces (lamellar morphology in Fig. 10). The dark solid line is the calculated critical velocity v_c (eq. (1)) as a function of particle size. The line gives the critical solidification velocity were the structure of the ice remains lamellar but the ceramic particles are engulfed by the moving ice interface leading to an isotropic microstructure.

4.2 Influence of solids content, freezing velocity and particle size on lamellae spacing

Above solidification velocities of $0.5 \mu\text{m}/\text{s}$, the ice shows a lamellar morphology with a lamellae spacing λ that can be described as a function of the solidification velocity v in form of a power law $\lambda \propto A \cdot v^{-1}$ (Fig. 4). The prefactor A includes the influence of solids content and particle size. With increasing solids content, A is increasing and the lamellae spacing is shifted to larger values as reported by Deville et al. [8]. The influence of particle size was shown in our freezing experiments for alumina suspensions with different median particle sizes of 0.25, 0.8 and $3.3 \mu\text{m}$ (Fig. 5). The experimental data show, that with increasing particle sizes the prefactor A also increases, shifting the lamellae spacings to larger values. Fig. 11 gives a map of lamellae spacing development as a function of particle size for a fixed solids content of 10 vol.%. The black curves show the measured data, while the dotted lines show the predicted lamellae spacings. For particle sizes of 4 and $6 \mu\text{m}$ the lamellae spacing development was estimated by the measured transition velocity from lamellar morphology to isotropic morphology by adjusting the prefactor A in the power law dependency.

At present, it is impossible to predict the lamellae spacing quantitatively due to the insufficient knowledge of particle system, solids content and solidification velocity. Never the less, using the model of instability formation based on supercooling effects, the influence of particle size, solids content and solidification velocity on the lamellae spacing can be explained and predicted qualitatively. This can be shown by using the analytically solvable model of Peppin et al. [18]. He gives a model for water based colloidal suspensions of polystyrene spheres. For water based alumina suspensions, there is no data available to forecast the lamellae spacing quantitatively up to now. To obtain these influencing quantities is the aim of present investigations.

Fig. 11 shows, that for a median particle size of $0.8 \mu\text{m}$ a lamellae formation can be observed up to highest examined solidification velocities of $700 \mu\text{m}/\text{s}$. Contrary to this investigations, the microstructure development for sintered ceramic bodies show a dense layer at the bottom of the sample, where the highest solidification velocities prevail [8]. It is not assumed, that the solidification velocities lie above $700 \mu\text{m}/\text{s}$ so for that reason, a lamellar microstructure has to be expected. To explain these differences we like to draw attention to two aspects: Very high solidification velocities are leading to a very fine lamellae structure. For that reason, the formation of a dense layer may either be a result of the coagulation of fine structures during sintering or caused by the influence of binder additives. Due to the presence of binder additives, the particles are hampered in there motion. This leads to higher drag forces and to the engulfment of the particles well below v_c , what was also observed in our experiments.

5 Conclusions & Summary

Based on the presented observations of the microstructure development of water based suspensions, the following conclusions can be drawn:

- (a) For very slow freezing velocities, ice grows planar, pushing the ceramic particles ahead of the solidification front. With increasing solidification velocities, the planar solidification front gets instable and a lamellar ice morphology is formed.
- (b) For small particle sizes, lamellar microstructures can be observed up to very high solidification velocities. With increasing particles size, the increasing drag forces reduce the mobility of the particles, leading to particle engulfment by the ice lamellae and an isotropic microstructure.
- (c) All publications known to the authors, discussing the microstructure development of the freeze-casting process with water as dispersion liquid, were carried out on sintered bodies

[7, 19, 20, 21]. For that reason, the microstructure development is not only affected by the solidification velocity, but also by binder additives and sintering artefacts. These factors must be considered in a discussion of the origin of the lamellar morphology.

- (d) Our measurements suggests, that the transition from planar ice growth to a lamellar ice morphology is due to particle-particle interactions as, to this time no transition was reported in literature for highly diluted suspensions. In this context, the lamellae formation can be predicted qualitatively, based on instability formation due to supercooling effects.

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Figures:

Fig. 1

Double-sided cooling setup (DS-setup) employed for directional freezing of the water based suspensions with constant solidification velocities. Pre-calculated temperature profiles allowed constant freezing velocities in a range from 5 to 30 $\mu\text{m/s}$ over a total sample height of 45 mm [16]

Fig. 2

Transition of the ice morphology from planar (A) to lamellar (B) shape as a result of the increased solidification velocity for a suspension with 5 vol.% alumina content. Images were taken perpendicular to the ice front, solidification started from bottom.

Fig. 3

Relationship between the transition velocity v_T for the transition from planar to lamellar ice morphology as a function of the solids content of alumina powder and for a polystyrene suspension with 5 vol.% polystyrene content.

Fig. 4

Lamellae spacing λ as a function of solidification velocity v for different alumina contents from 5 to 30 vol.% for a median particle size of 0.8 μm .

Fig. 5

Lamellae spacing vs. solidification velocity for different alumina particle sizes for a solids content of 10 vol.%. The measurements for CT3000SG (grey curve) were realized with single side cooling experiments (see Fig. 4), measurements of AA-03 and AA-3 (black curves) were realized with double side cooling experiments at constant solidification velocities.

Fig. 6

SEM image of an unidirectionally frozen droplet of alumina suspension with solids content of 20 vol.%. The solidification velocity was $\sim 250 \mu\text{m/s}$

Fig. 7

(A) Influence of particle size on solidification velocity v and microstructure development for alumina and polystyrene suspensions with particle sizes between 0.8 μm and 15 μm . (B) SEM images of microstructure development for polystyrene particle sizes of 4.1 and 6.6 μm for solidification velocities under and above the critical solidification velocity.

Fig. 8

Schematical overview of microstructure development for suspensions with low solids content (no particle-particle interactions) and high solids content (particle-particle interactions).

Fig. 9

Influence of particle size on the microstructure development as function of solidification velocity. Grey lines: Calculated critical velocity v_c from Eq. (1) for different temperature gradients.

Fig. 10

Map of microstructure development in linear dependence of particle size and logarithmic dependence on solidification velocity for water based suspensions. Dark points and lines: measured data; dashed lines: predicted values.

Fig. 11

Map of the lamellae spacing in dependence of particle size from very slow up to very fast solidification velocities for water based suspensions. Dark lines: measured data; dashed lines: predicted values.

Tables:

Table I.

Different particle systems used in the investigations