6. Discussions

6.1 Discussions of rheological properties on the starting slurries and the dependence on porosity as well as the pore size distribution

The analysis performed in the previous section (especially porosity and pore size distribution) shows how the particular microstructures of the porous materials may be affected by the solid load content. Therefore, it is advisable to study and discuss the role of solid load content on starting slurry characteristics and especially porosity, pore morphology and pore size distribution. Good knowledge and understanding of these parameters will enable to design an optimal control of pore characteristics.

The rheological measurements showed pseudoplastic behaviour of the slurries, indicating a well-dispersed solid phase in the suspension (see Chapter 4.1.2). The rheology of the starting slurries varies significantly depending on solids contents.

Density measured at 25°C and porosities, for samples frozen at –25°C and a distance from cooling plate of 1cm, versus slurry solid load content are presented in Fig. 6-1.

*Fig. 6-1: Density and porosity in dependence of slurry concentration*
From this figure it can clearly be seen that the starting slurry density increases with increasing slurry concentration. This is in accordance with less liquid phase in the suspensions. In case of decreasing slurry concentrations large pores can be obtained and because of the lower viscosity the slurries can be easily handled. On the other hand it will decrease the mechanical properties of the obtained materials. The increase of volume fraction of solids, hence less water, determines the created, materials after freezing, hence the degree of porosity as shown in Fig. 6-1. The obtained pores result from the ice crystals and the porosity of the particles themselves, which is of less significance. Furthermore, a good control of the starting slurries physical properties such as density can promote a route to control porosity as well as the pore size. In Fig. 6-2 are micrographs presented, of cross sections perpendicularly to the ice growth direction, showing the microstructural evolution of samples frozen at -25°C. No cracks or defects have been observed. The change in the pore size results only from different solid load contents, because all other parameters have been kept constant. These pores shown in Fig. 6-2 are generated after sublimation of the ice crystals. By increasing slurry concentration many water molecules are bond to the particle surface [Sof01].

Fig. 6-2: Cross sections (a, b, c 40 Vol. % solid load; d,e,f 36 Vol. % solid load), a-d 5 cm distance from cooling plate: b-e 3 cm and: c-f 1 cm
Increase of density and viscosity by increasing slurry concentration leads to formation of aggregates for a ceramic skeleton formation, which is formed due to the freezing. The bigger the aggregates are the greater are the possibilities to settle due to gravitational forces. The same behaviour has been observed by Terpstra et al. [Ter95]. Therefore, the suspensions have been electrostatic stabilized by using Polyacrylic acid. By this way the pH of the suspensions has been shifted between the Isoelectric Point (IEP) of Al2O3, which is between 8-9 and SiO2 between 2 and 3 [Ree88]. Lange et al. [Cha91, San00] reported on an aqueous alumina– zirconia suspensions in which the pH was shifted between IEP of the both materials. The aggregation did lead to a mixture of the both materials that was not disrupted during consolidation.

Since ceramic particles with different sizes have been used (see chapter 3.1) a better degree of packing between the ceramic particles can be expected. Increasing the size of the used particles leads to an increasing permeability. Therefore, large amounts of water stays closed in such a spaces and voids of the aggregates. Due to the incorporation of water the mass transport in the suspension volume becomes more difficult. The “locked” amount of water cannot easily be taken out due to the physical resistances and does not take place in the continuous macropores formation process (see Fig. 6-3).

Fig. 6-3: Schematic view of aggregates for ceramic skeleton formation
Fig. 6-4 shows the density difference according to the distance from the cooling plate. The data on the samples after the freezing have been obtained by mercury intrusion porosimetry. Densities of the samples have been found to increase linearly with decreasing distance from the cooling plate. This can be attributed to a settling of the particles to the bottom. In a freeze-casting process two processes are competing with each other. First the ice crystals are stimulated to grow from bottom to the upper face in vertical direction because of the temperature gradient. On the other hand the ceramic particles settle because of their weight. In case of low freezing, respectively slow crystal growth rates large crystals will be formed. There might exist a place at which the freezing front will meet a particle front. Such an effect has been observed when the slurries were frozen at –5°C. The bottom and the upper phase of the samples were very hard. Between them only a crumble phase has been observed. The samples have been very brittle and not suitable to a processing even at the highest solid load contents.

Fig. 6-4: Samples density in dependence of distance from cooling plate.

Freezing temperature –25°C
Fig. 6-5 shows the results obtained for starting slurry densities in dependence of solid load contents. The plot shows the density values obtained from mercury intrusion porosimetry. From the figure it can be seen that all curves follow the same manner when increasing suspension concentration. Also the differences between starting slurry density and after the freezing have found decreasing with lower solid contents. At the upper face the density was found with only a little margin to the starting slurry density. This result is another evidence for the fact that particles settling. Low slurry concentrations correspond to more water, respectively, more free space for particle movements. Also the possibility for particle interactions is less therefore less agglomeration happens. With increasing solid load the difference between the densities of the frozen samples decreases.

![Graph showing starting slurry density and density after freezing in dependence of solid load content. Freezing temperature -25°C](image)

**Fig. 6-5: Starting slurry density and density after freezing in dependence of solid load content. Freezing temperature -25°C**

At the highest solid load content the samples exhibit almost no density gradient. This result can be attributed to a better dispersion of particles in the suspension volume. The density of the samples has been measured by the Archimedes method. The
samples were positioned in a measurement cylinder with known amounts of water and the cylinders were covered to prevent water evaporation. After 24h the water level was measured and from the level margin of the samples the density was calculated. A good agreement in the values between Archimedes method and the results obtained by mercury intrusion porosimetry has been found. Therefore, it has been concluded that most of the pores are open pores or interconnected ones.

6.2 Discussions on contact angle, interfacial tension and nucleation kinetics

According to the classical theory the nucleation process requires that the nucleus overcomes a certain Gibbs energy barrier [Mul01]. These nucleuses are aggregates formed of water molecules, which are transformed to solid state, ice. Eq. 2.2 gives the Gibbs energy change. In this equation the interfacial energy is a very important factor. The interfacial energy is a function of temperature, because the interfacial energy is related to the surface energy of the substance [Bal98], and the surface energy is dependent on temperature. Therefore, it needs to be taken into consideration. According to Haasner [Haa02] and Na [Na03] a change of materials roughness will result in change of the contact angle respectively in interfacial energy. Such a change can be attributed to an increase of the contact area between substrate and new-formed phase Fig. 6-6.

\[
\cos \theta = r_f \frac{\sigma_{sl} - \sigma_{cs}}{\sigma_{cl}}
\]  

(6.1)

Roughness can be taken into account by using Wenzel’s equation.
Wenzel uses Young’s equation and applies a correction factor \( r_w \) were \( r_w \) is divided as actual surface area to the planar surface area. The Wenzel equation means that a surface with a higher roughness will lead to an increase of the wetting angle. In the previous chapter the results of contact angle measurements in dependence of the cooling surface have been presented (see Chapter 5.2.1.2). Four surfaces with wide ranges of roughness have been investigated (see Fig. 6-7). An effect on contact angle in dependence of cooling surface roughness has not been observed in the presented results (see Fig. 6-12). According to Mullin [Mul01] in case of increasing the contact angle an increase of the energy required for nucleation can be expected and will shift the system energy toward homogeneous nucleation (see Fig. 5-25), which requires higher energies and is not favourable. Fig. 6-7 shows the energetic margin between homogeneous and heterogeneous nucleation for rough steel surfaces. From this figure it can be seen that the energy requires for heterogeneous nucleation is obviously lower.

Fig. 6-7: Free energy versus supercooling for rough steel surface and slurry with 36 Vol.% solid load
Fig. 6-8: Contact angle measurements for suspension with 36 Vol.% solid loads on different cooling plate surfaces

As previously noted, in Chapter 5.2.1.2, each reported contact angle was measured several times at different points on the same surface and averaged. The differences in contact angles obtained from different cooling surfaces are shown in Fig. 6-8. In each case the data exhibit the same general temperature dependence behaviour of increasing contact angle by decreasing the operating temperature. The standard deviation for contact angle measurements was less than 5% of the averaged values at each cooling surface. The measured contact angle shows little variations with changing the cooling surface material and temperature as the main parameter affecting contact angle. From the figure it can be seen that only a small difference of the contact angle has been obtained in dependence of the plate material or roughness. The same results also have been achieved for the interfacial tension. Fig. 5-17 clearly shows that the interfacial tension is influenced by material and only a little deviation have been observed by roughness changes.
The averaged values have been used to calculate the f-function needed to obtain the free energy values for heterogeneous nucleation (Eq. 2.9 and 2.8). Fig. 5-25 shows the calculations obtained of the f-function, Eq. 2.9. As can be seen all curves have the same behaviour and lie on almost the same place. According to classical nucleation theory by changing surface or surface properties each curve should have an own character. Therefore 4 different surfaces, materials and roughness, have been investigated and used as cooling plates. As can be seen from the Fig. 5-25 the effect of the f-function obtained from different cooling plate materials have not been observed. In case such effects exist they are too small to be detected. From here it can be concluded that the cooling surface material and properties play an almost insignificant role in state of design and control of nucleation.

Fig. 6-9: Porosity for suspension with 36 Vol.% solid load and 1cm distance from cooling surface in dependence of cooling plate material

Fig 6-9 shows the changes of porosity in dependence of cooling plate material. In case the cooling surface influences the nucleation process it will affect the critical nuclei size. As presented above the porosity is strongly dependent on the ice crystals size. Therefore, difference in the porosity values near the cooling surface should be
achieved. As can clearly be seen significant changes in porosity values have not been observed even by changing the freezing temperature. The deviations in the values correspond to the measurement errors. The same results have been obtained for the pore radii presented in Fig. 6-10.

![Graph showing average pore size in dependence of cooling plate material and freezing temperature.](image)

**Fig. 6-10:** *Average pore radius for suspension with 36 Vol.% solid load and 1cm distance from cooling surface in dependence of cooling plate material*

In Fig. 5-42 results for porosity values are presented in dependence of moulding form materials. From the figure it can be seen that both curves follow the same manner and the deviation in results is about 3-5% which can be accorded to the measurement errors.

Fig. 5-54 shows the experimental results for pore size distributions obtained for suspensions with the same solid load content and frozen at the same temperatures where only the moulding form material varies. Small differences in pore radius values have been detected but are in a good agreement according to the measurement mistakes. Evidently it is shown that the moulding form material does not significantly affect the pore size distribution even near the cooling plate surface.
If the nucleation process starts on the moulding form surface change in porosity and pore size distribution should be detected in the state of obtaining the critical nuclei with different sizes. From the presented results such a difference has not been observed. From all above presented results it can be concluded that the nucleation process is almost independent of the cooling plate and the moulding form material and properties. Therefore, it has been supposed that nucleation occurs on ceramic particles surface. Padilla and Talanquer [Pad01] reported that in case of heterogeneous nucleation of supersaturated vapours on spherical aerosol-like substrates the work of formation for the critical nucleus increases when the radius of the aerosol particles decrease in a given supersaturated vapour. According to this statement it can be supposed that in case of the presence of two materials with different particle size, for Al₂O₃ 700nm and for SiO₂ 14nm in diameter, the nucleation process will occur on the alumina particles surface because it is energetically preferable. From the literature it is known that the alumina particles are very hydrophilic. Therefore a building of a surrounding layer of the water molecules can be expected. The information obtained from the company shows that the alumina particles have a total porosity of 59.4%, surface area 60-80 m²/g and an average pore diameter 3.5nm. Such conditions of high surface area, porous structure, therefore high roughness can be considered as optimal conditions for heterogeneous nucleation. The particle surface has been studied by SEM. Figs. 5-44 and 5-45 show alumina and silica particle surfaces, respectively. From the micrographs it can be seen a very rough and porous surface of the alumina particles while the silica particle surfaces is smoother and only some cracks have been observed. By using Fletcher's and Gorbunov's theory it can be predicted that nucleation occurs inside the particle pores. Fig. 6-11 shows the results obtained for crystal growth in dependence of the volume fraction of solids. As can be seen the volume fraction of solids strongly influences the crystal growth where by increasing the solid volume fraction crystal growth exponentially increases. Such results have been observed at all freezing temperatures and distances from the cooling plate. This result can be attributed to less water, which needs to be crystallized, due to increasing solid loads. The time needed for nucleation and complete sample freezing (crystallization) is reduced because the ceramic particles are “inert” for the crystallization process. Fig. 6-12 shows the time needed for nucleation obtained from the cooling curves (see Fig. 5-28).
Fig. 6-11: Crystal growth rate for suspensions frozen at $-25^\circ$C and distance from cooling plate 1 cm

Fig. 6-12: Time needed for nucleation obtained for slurries cooled with 0.08 K/min
The time has been determined from time and temperature at which nucleation occurred until the system reach a stable cooling regime again. This result can be accorded to a better thermal conductivity inside the suspensions by increasing the solid load content. Thermal conductivity is the property that determines the working temperature levels of a material, and it is an important parameter in problems involving steady state heat transfer [Sant00]. Fig. 6-13 presents the thermal conductivity for all components in the slurries. From the figure is clear to be seen that alumina is the component, which continuously increase its thermal conductivity at decreasing temperature. Silica slightly decreases his thermal conductivity at temperature decrease. It is also apparent that two different regions can be identified for water. In the first region the thermal conductivity is decreasing by decreasing temperature down to 0°C. Region two starts at 0°C were a step appears at the water freezing temperature (crystallization starts) and ice thermal conductivity increase by decreasing temperature. In the second case a better and faster thermal distribution inside the slurries can be achieved.

![Fig. 6-13: Thermal conductivity for the slurries components](image)

*Fig. 6-13: Thermal conductivity for the slurries components*
Crystal growth rate is temperature dependent as it was shown in Fig. 5-33. Driving force for the growth of ice crystals was found to be the temperature difference between the cold side (moulding form bottom) and the warm side (moulding form upper side), therefore an increase in the slurries thermal conductivity will result in faster growth.

In Fig. 6-14 are the calculated values for thermal conductivity plotted at various temperatures and solid load contents in the slurries. Apparent is that the thermal conductivity is strongly influenced by solid loads and slightly increase by decreasing temperature.

![Fig. 6-14: Thermal conductivity for different slurries at various temperatures](image)

From the economical point of view higher crystal growth is preferable [Kim01]. An increase of solid load content and decrease of freezing temperature will cover such a request. Also by increasing of solid load content and increase of mechanical stability of the products can be expected. For all industrial needs an optimum between solid loads and obtained porosity, as well as pore size distribution needs to be found according to the desired properties.
6.3 Porosity and pore size distribution

Fig. 6-15 (a) shows optical micrograph of porous samples taken at different distances from cooling plate prepared from slurry with 36 Vol.% solid loads and frozen at –15°C. The pores are distributed uniformly throughout the whole sample. That three-dimensional structures have been obtained can be seen by the micrographs of the next layer. The micrographs shows that the pores have a well-defined shape even by changing the distance from cooling plate or, as mentioned in the previous chapters, pore size gradient have been obtain in dependence of distance from cooling plate. The pores obtain their morphology from ice crystals. Therefore it was reasonable to suppose that there exists a dependence between pore size and crystal growth.

Fig. 6-15: Micrographs taken from samples cross sections perpendicularly but different distances from the cooling plate to the ice crystals growth direction for slurry with 36 Vol.% solid load frozen at –15°C. Micrograph (a) correspond to 5cm distance from cooling plate, (b) 4cm, (c) 3cm and (d) 2cm
Fig. 6-16: Crystal growth rate, macro and mesopores in dependence of distance from cooling plate for slurry with 36 Vol.% solid load frozen at –15°C

Fig. 6-16 shows the dependency between crystal growth rate, macro and mesopores average radius and distance from cooling plate. It is apparent that the average pore radius is strongly dependent on the crystal growth rate. By decreasing the growth rate the pore radius increases. In Fig. 6-17 the pores radius is presented versus the crystal growth rate for slurry with 36 Vol.% solid loads frozen at different temperatures. An exponential decrease has been recognized for all curves. Generally it is known that at low crystal growth rates, respectively low temperature gradients, crystals with bigger sizes are build. This result indicates that the pore radius can widely be controlled by managing crystal growth. Therefore a good control of the temperature gradient between bottom and upper face of the moulding form needs to be achieved. The same behaviour has been observed for the investigated slurries at all freezing temperatures at all used cooling surfaces. From Fig. 6–17 also it can be seen that the increase of pore radius is greater at lower freezing temperature, therefore an increase of the pore size gradient has been observed. On the other hand processing at such a “high” temperature is not recommended from the industrial point of view because it takes too much time, (as has been shown in the previous chapter) for a complete freezing of the samples. In case such a pore size or pore
gradient needed a decrease of the products thickness or an increase of the solid load content is recommended. Also an overloading with solids is not recommended because in this a case lot of water molecules will be bond on the ceramic particle surfaces or will be incorporated inside the aggregates, which can cost elimination of the freezing process.

Fig. 6-17: Macropores average radius in dependence of crystal growth rate for a slurry with 36 Vol.% solids frozen at different temperatures

The dependence between an average pore radius and the obtained porosity has also been investigated. Fig. 6–18 illustrates the effect of the pore radius and the porosity in dependence of distance from cooling plate. From the figure it can be seen that with increasing the average pore radius the porosity decrease. This is in accordance with the volume of the created pores. Small pores have a higher surface therefore higher cumulative volume, which results in an increase of the degree of porosity. The results are presented in Fig. 6-19. The data presented above show that controlling the temperature gradient could control the average pores radius. Therefore the composition of the slurries and the freezing parameters are the key parameters, which determine the resulting pore size and morphology as well as the final porosity.
**Fig. 6-18:** Macropores average radius in dependence of porosity for a slurry with 36 Vol.% solids frozen at –25°C

**Fig. 6-19:** Macropores cumulative volume and total specific surface area for a suspension with 36 Vol. % frozen at –25°C
All results presented here are for macropores. Also for mesopores the same parameters dependences have been observed. Fukasawa et al. [Fuk01, Fuk01a] reported that the mesopores disappeared when sintering was applied. Therefore all investigations here have been focused on the macropores development.