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Obtención de cerámicos a base de caolín mediante el proceso de Freeze casting

MATERIALS ENGINEERING

Kaolin based ceramics obtained by Freeze casting process

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Resumen

El proceso de Freeze casting ofrece la oportunidad de obtener materiales sintéticos que imitan características microestructurales de materiales naturales como el hueso y el nácar. Estos materiales se caracterizan por presentar una buena combinación de resistencia y tenacidad; propiedades deseables en materiales sintéticos de ingeniería. El proceso de Freeze casting consiste en cuatro pasos. Primero, preparación de una suspensión coloidal de partículas cerámicas, en este trabajo se utilizaron suspensiones a base de caolín y agua con diferentes concentraciones de caolín. Luego de preparadas las suspensiones, se realizó un proceso de congelamiento direccional que brinda las características microestructurales de la parte final, obteniendo poros alineados debido a la formación direccional de los cristales de agua que mueven las partículas cerámicas alrededor de ellos, creando distintas tipologías de poros. En este trabajo se varió la velocidad de enfriamiento del proceso. Después de congelada la suspensión coloidal de partículas cerámicas se realizó un proceso de liofilización el cual cambia la fase sólida del agua, obtenida del proceso de congelamiento, a gas sin pasar por estado líquido, permitiendo que la parte mantenga la forma de los cristales de agua. Finalmente, se realiza el proceso de sinterizado. Resultados del análisis microestructural de las muestras obtenidas revela que la variación de la concentración de partículas cerámicas en la suspensión coloidal y la variación de la velocidad de enfriamiento en el proceso de solidificación tiene un efecto considerable sobre la microestructura obtenida. Las microestructuras varían desde poros columnares hasta poros esféricos.

Palabras clave: *Caolín, freeze casting, materiales bioinspirados, microestructura.*

Abstract

Freeze casting offers a tremendous opportunity to obtain bio-inspired synthetic materials that mimic microstructural characteristics of natural materials like bone and nacre. These natural materials display high strength and toughness; properties usually desired in synthetic engineering materials. The freeze casting process involves four basic steps. The ceramic slurry preparation consists of fine ceramic particles that are suspended in a fluid. In the current work, water based kaolin suspensions were prepared varying the volume fraction of ceramic particles. After the ceramic slurry is properly prepared, the slurry is frozen. The solidification process is often performed using directional freezing, which creates laminar pores, providing the microstructural characteristics of the final part. When a crystal is formed the frozen front moves the particles around it, allowing particles to agglomerate around the crystal, creating different types of pores. In the present study, freezing rates were varied. Subsequently, the samples have to be lyophilized in order to sublimate the frozen liquid phase. Sublimation is the transformation of a solid phase directly to the gas phase. As a result the lyophilized sample has a porous structure with a replica of the water crystals formed during freezing. As a final step, sintering of ceramics is performed. Results of the microstructural characteristics of the samples revealed that varying the volume fraction of ceramic particles and freezing rates have a direct influence on the pore characteristics, changing from circular to laminar pores.

Keywords: *Bioinspired materials, freeze casting process, kaolin, microstructure.*

1. Introduction

Materials have different functions in nature. For instance, bone is used in structural applications whereas nacre is used as a protective material. Bio- inspired materials are materials that mimic one or more aspects of natural materials (Meyers et al., 2013; Chen et al., 2012; Meyers et al., 2008; Launey et al., 2009). In order to obtain bio-inspired (synthetic materials), scientists have explored different methods of manufacturing, by investigating the scientific report of Malshe et al. (2013) it is possible to find a large list of other processes aimed to mimic natural materials features.

Freeze casting offers a tremendous opportunity to mimic some natural materials with synthetic materials that could lead to the development of novel structures for engineering applications. There have been initiatives using freeze casting to produce bio-inspired materials for bone replacement (Deville et al., 2006; Yang et al., 2010; Pawelec et al., 2014). Additional studies on freeze casting have been devoted to the manufacture of parts mimicking some characteristics of nacre with high strength and toughness by infiltrating the structures with a second face (Munch et al., 2008; Sinchuk et al., 2013; Liu et al., 2014; Shaga et al., 2015).

In general, the freeze casting process consists of four basic steps illustrated in Figure 1. i) The slurry preparation consists of any material in the form of particles suspended in a fluid, usually water, camphene and tert-Butyl alcohol based, each of them producing different pore structures, leading to different characteristics of the material produced. ii) Solidification, the slurry is frozen. Depending on the solvent used in the slurry preparation, the crystals formed during freezing will have different shapes. The crystals are formed using directional freezing, which creates laminar pores (Deville., 2008). Water can be used as a solvent to produce dendritic shaped crystals, resulting in elliptic pores with lengths between 30um and 500um (Fukasawa et al., 2002). iii) Sublimation, the samples have to be lyophilized in order to sublimate the frozen liquid phase. Sublimation is the transformation of a solid phase directly to the gas phase. As a result the lyophilized sample has a porous structure with a replica of the crystal's shape formed during freezing. iv) Finally, sintering is performed in a furnace.

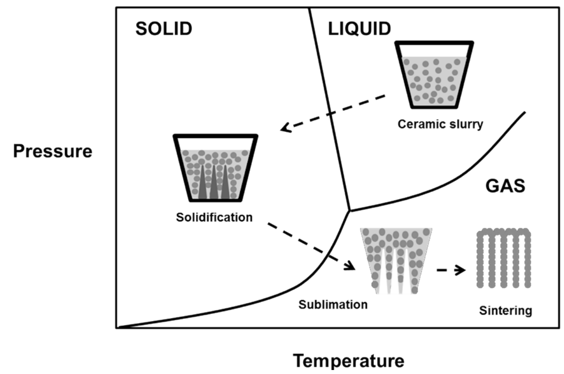

Figure 1. *The freeze casting process consists of four basic steps. 1. Ceramic slurry preparation 2. Freezing the ceramic-solvent system. 3. Sublimation of the frozen solvent. 4. Sintering.*

Applications of material obtained by freeze casting may include ceramics for gas cleaning (Kitaoka et al., 2004), catalysts supports (Pham-Huu et al., 1999), drug delivery systems (Szepes et al., 2007), sound absorbing ceramic materials (Frank et al., 2011), among others. A recent review article by Hammel et al., (2014) gives a good summary of different applications of porous ceramics. The aim of the current study is to evaluate the effects of kaolin volume fraction and freezing rates on the microstructure of the sintered parts obtained by freeze casting.

2. Materials and methods

Freeze casting requires a set of materials to prepare the ceramic slurry. In the current study the aqueous medium used was distilled water as it has been successfully used in previous studies (Launey et al., 2009; Liu, 2011). The Kaolin ($Al2Si2O5(OH)4$) employed was obtained from Protokimica S.A.S with average particle size of 17.886 μm and specific surface area of 0.569 m2/g (Mastersizer 2000). The slurry was then prepared with different Kaolin content (10, 30 and 50 %Weighted). The procedure to prepare the ceramic slurry consisted of weighing

(Mettler Toledo ML204/1, d=0,1 mg) the precise amount of distilled water, kaolin, and an organic defloculant (polyvinylalcohol, 1,4 wt % of the kaolin powder, 341584 ALDRICH Poly (vinyl alcohol), Mw 89,000-98,000. The organic defloculant was added to rise the stability of the kaolin suspension via adsorbed organic molecules around the particle surface (Chaiwong & Nuntiya., 2008). Further, Poly(vinyl) alcohol works as a binder, increasing the strength of the green part (Launey et al., 2009). After weighting, the distilled water and organic binder were mixed at 700 RPM in a magnetic stirrer/hot plate (Corning PC-420D) at 80 oC for 12 hours to dilute the Poly(vinyl alcohol). When this blend reaches room temperature (20 °C) the ceramic powder is added gradually while it is kept under constant mixing. To ensure a good dispersion the slurry must be mixed for about 24 hours (Liu., 2011). The kaolin slurry was left at its inner pH 6.0 because it was more stable at such value (Chaiwong & Nuntiya., 2008).

The freezing apparatus used is described by (Liu., 2011). Three different freezing rates where used to freeze the slurry (e.g.: 0,019 (V1), 0,025 (V2) and 0, 081 (V3) mm/sec) to study its effects on the final microstructure. The kaolin slurry was poured into a precooled acrylic mould of 10 mm in diameter, 50 mm in length and thickness of 20 mm. After freezing, the part was freeze dried for 12 hours to allow the ice to sublimate (Preiss et al., 2012) (VirTis BenchTop 4K, 16 mTorr at -80 °C). Sintering was then performed in a convective furnace (Nabertherm LT 15/13/P330) at 1300 °C for three hours. The porosity of the samples was assessed by optical microscopy on reflection mode to study the pore morphology (Zeiss Discovery.V8). Finally, the bulk density of the samples was measured using paraffin coating and the Archimedes' method.

3. Results and discussion

Results showed that the samples displayed three well-defined zones as shown in Figure 2, each having different pore morphology. The bottom of the sample which is in direct contact with the cooled surface shows a denser cellular structure with no visible macro-porosity. This is the result of the initial super-cooling effects of pouring the ceramic slurry over a cold surface, leading to a not steady freezing (Waschkies et al., 2011). Just above such zone, there is a transition where the aligned pores begin to get formed which is produced by the instability of the water crystals while changing from cellular to lamellar structures (Deville et al., 2006). Finally, towards the top of the sample appear well defined lamellar macro-pores that get wider in the direction of the upper region. The pores are aligned towards the freezing direction with a branch-like structure. Lamellar macro-pores are the consequence of slower freezing front at the top of the sample resulting in a homogeneous ice nucleation (Schoof et al., 2001). The pore gradient characteristics reported here have also been described by several authors (Moritz & Richter., 2007; Sofie., 2007; Waschkies et al., 2011). As lamellar pores are the most important feature expected from freeze casting, the subsequent analysis will be concentrated on this region.

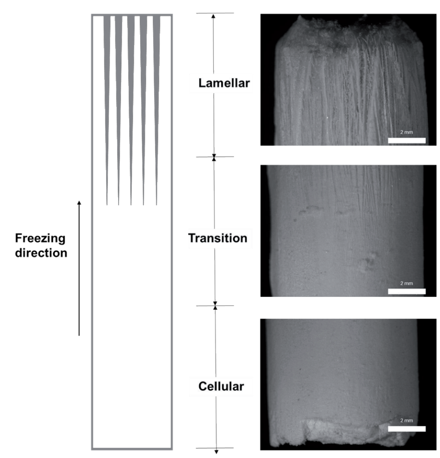

Figure 2. *Distinctive samples characteristics. Three typical zones with length dependent on slurry solid content and freezing rates.*

The lengths of the three main regions are dependent on the freezing rates and solid fraction content. To assess these characteristics, the length of the lamellar macro-pores (top of the sample) respect to the total length of the sample was analyzed, as shown in figure 3. In general, slow freezing rates promote the formation of lamellar structures within the sample, resulting in longer lamellar structures. As freezing rates increase, the length of the lamellar structures tends to decrease. The lamellar structure forms as a result of particle-frozen front interactions. Slow freezing rates produce a slow frozen front. Then, the crystals that are forming while the freezing front is advancing are able to move the particles around them, allowing the formation of lamellar structures. On the other hand, high freezing rates do not allow the particles to be moved around the crystal, finishing trapped within the water crystals, hence not permitting the formation of lamellar pores (Rempel & Worster., 1999; Rempel & Worster., 2001). Therefore, selecting the appropriate freezing rate has a direct effect on the formation of lamellar structures within the sample. Particle size is an important feature to take into account when analyzing the microstructure obtained. For instance, Deville et al., (2009) noticed that using submicron particles size results in the formation of crack like defects affecting the compressive strength of the samples.

Waschkies et al., (2011) studied the influence of particle size and freezing rates on the microstructure using different alumina particle sizes in a water based polystyrene medium. Results show that when the particles size is around 2µm lamellar structures are obtained in a wider range of freezing rates (1-1000 µm/s). However, when larger particles (15µm) are used, lamellar structures are only formed at freezing rates below 3µm/s. Results found in the current study are not in agreement with those by Waschkies et al., (2011). Here, the slowest freezing rate was 19µm/s using an average particle size of 17,886 µm. Lamellar structures were obtained only after completing the process. As mentioned by Deville, (2010) one of the main challenges of comparing freeze casting results is that the pore morphology can be varied by using different additives. For instance, Zhang et al., (2009) observed that the pore morphology and size is significantly affected by the addition of gelatin to the ceramic slurry. Fu et al., (2008) added glycerol – water mixtures and concluded that the glycerol produces finer pores. Thus, the results obtained here might not match with the ones by Waschkies et al., (2011) because the ceramic slurry were prepared using different base material, medium and additives.

Solid fraction also has a direct effect on the length of the lamellar structure. For instance, samples with high solid fractions tend to have a longer lamellar zone at slow freezing rates, whereas at high freezing rates they show the tendency to have shorter lamellar zones. For particle-fluid mixtures the thermal properties depend on parameters like thermal conductivity of the base fluid and particles, volume fraction and temperature of the system, among others (Wang & Mujumdar., 2007). The thermal conductivity of kaolin clay (0,3 W/m-K) (Etuk et al., 2003) is lower than for water (0,59 W/m-K). As a result, higher solid fractions end up in a lower thermal conductivity of the ceramic slurry, which slows the freezing front through the sample, resulting in a faster homogeneous ice nucleation which creates longer lamellar structures. According to Deville et al., (2007) solid fractions higher than 80 wt % make that the lamellar structure get lost and the pores are not interconnected.

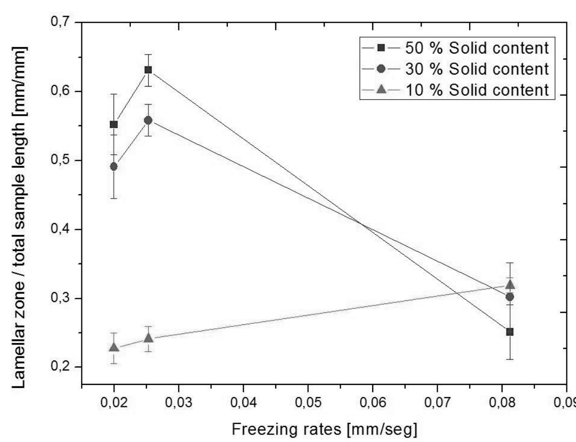

Figure 3. *Lamellar zone length with respect to total sample length at different freezing rates and solid fractions. The error bars indicate standard deviation.*

Figure 4 shows the pore morphologies at different freezing rates and solid fractions. The freeze casting process is highly reproducible, giving the opportunity to control structure formation by simply tuning the freezing rates and solid fractions of the slurry. At 10 % solid content (figures 3a, 3b and 3c) the sintered kaolin part barely forms crystals. However, at slow freezing rates it was found a lamellar structure. At 10 % solid content during freeze-drying, approximately 60% of the poured sample length collapsed due to the lack of interactions between particles. The remaining 40 % of the sample showed the characteristics previously described. Deville et al., (2007) also pointed out that at low ceramic content the green body becomes weaker and difficult to handle. Nonetheless, it can be improved by increasing the binder content. The length and size of the lamellar pores at slow freezing rates at 30 % and 50 % solid fractions are noticeable increased as observed in figures 3d, 3e, 3g and 3h. At 30 % the lamellar pores are well defined along the sample with a remarkable porosity. Higher freezing rates certainly do not promote the formation of well-defined crystals at any solid content (figures 3c, 3f, and 3e). Results of density of the lamellar zone at different freezing rates and solid fractions are shown in figure 5. Overall, for higher solid fractions are obtained higher densities of the lamellar structure of the samples, as well as slow freezing rates give time to the particles to sediment, thus the density of the top of the sample tend to be reduced; explaining the lamellar zone characteristics at different freezing rates and *solid contents.*

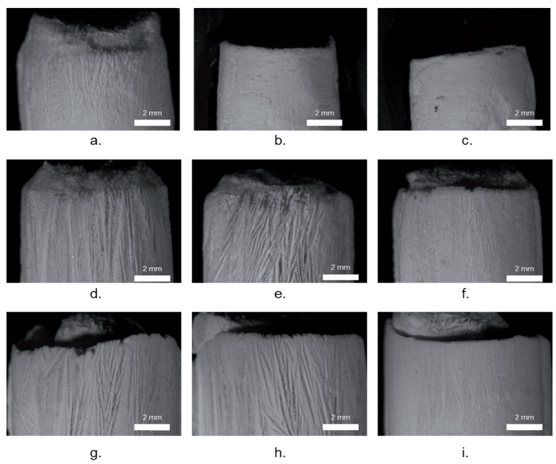

Figure 4. *Lamellar zone characteristics at different freezing rates and solid content. a. 10% solid content at 0,019 mm/sec. b. 10% solid content at 0,025 mm/sec. c. 10% solid content at 0,081 mm/sec. d. 30% solid content at 0,019 mm/sec. e. 30% solid content at 0,025 mm/sec. f. 30% solid content at 0,081 mm/sec. g. 50% solid content at 0,019 mm/sec. h. 50% solid content at 0,025 mm/sec. i. 50% solid content at 0,081 mm/sec.*

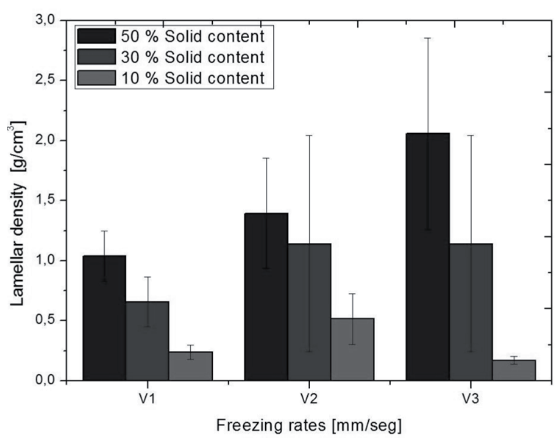

Figure 5. *Density of the lamellar zone at different freezing rates and solid content. The error bars indicates the standard deviation.*

4. Conclusions

The freeze casting process is a highly reproducible process giving the opportunity to control the porous structure formation by simply tuning the freezing rates and solid fractions of the slurry. A study of the microstructural characteristics of the samples revealed that varying the solid fraction of ceramic particles and freezing rates have a direct influence on pore morphology.

In general, slow freezing rates promote the formation of lamellar structures at the solid fractions evaluated (10 %, 30 % and 50 %). Nonetheless, the samples showed a lower density due to the sedimentation time given to the particles during the freezing process. The best defined and longer lamellar pores were obtained at 30 % solid content at slow freezing rates. When the solid fraction is increased to 50% there are still lamellar structures but the samples showed a higher density and the lamellar pores were not well defined. At 10 % solid fraction the samples presented several problems during freeze drying due to the lack of particle interactions, as a consequence the initial poured sample length was reduced about 60% after the freeze drying process. Thus, solid contents as low as 10% are not recommended in freeze casting processes unless such characteristics are desired. Finally, higher freezing rates certainly do not promote the formation of well-defined longer crystals at any of the solid contents evaluated and the samples showed higher density.

5. References

Chaiwong, N. & Nuntiya, A. (2008) Influence of pH, electrolytes and polymers on flocculation of kaolin particle. *Science* 35 (1), 11-16.

Chen, P.Y., McKittrick, J. & Meyers, M.A. (2012) Biological materials: functional adaptations and bioinspired designs. *Progress in Materials Science* 57 (8), 1492-1704.

Deville, S. (2008) Freeze-casting of porous ceramics: a review of current achievements and issues. *Advanced Engineering Materials* 10 (3), 155-169.

Deville, S. (2010). Freeze-casting of porous biomaterials: structure, properties and opportunities. *Materials* 3 (3), 1913-1927.

Deville, S., Maire, E., Bernard-Granger, G., Lasalle, A., Bogner, A., Gauthier, C. & Guizard, C. (2009). Metastable and unstable cellular solidification of colloidal suspensions. *Nature materials* 8 (12), 966-972.

Deville, S., Saiz, E., Nalla, R.K. & Tomsia, A.P. (2006) Freezing as a path to build complex composites. *Science* 311 (5760), 515-518.

Deville, S., Saiz, E. & Tomsia, A.P. (2007). Ice-templated porous alumina structures. *Acta Materialia* 55 (6), 1965-1974

Etuk, S.E., Akpabio, I.O. & Udoh, E.M. (2003). Comparison of the thermal properties of clay samples as potential walling material for naturally cooled building design. *Journal of Environmental Sciences* 15 (1), 65-68.

Frank, G., Christian, E. & Dietmar, K. (2011). A novel production method for porous sound absorbing ceramic material for high temperature applications. *International Journal of Applied Ceramic Technology* 8 (3), 646-652.

Fu, Q., Rahaman, M.N., Dogan, F. & Bal, B.S. (2008). Freeze casting of porous hydroxyapatite scaffolds. I. Processing and general microstructure. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 86 (1), 125-135.

Fukasawa, T., Deng, Z.Y., Ando, M., Ohji, T. & Kanzaki, S. (2002) Synthesis of Porous Silicon Nitride with Unidirectionally Aligned Channels Using Freeze-Drying Process. *Journal of the American Ceramic Society* 85 (9), 2151-2155.

Hammel, E.C., Ighodaro, O.R. & Okoli, O.I. (2014). Processing and properties of advanced porous ceramics: An application based review. *Ceramics International* 40 (10), 15351-15370.

Kitaoka, S., Matsushima, Y., Chen, C. & Awaji, H. (2004). Thermal cyclic fatigue behavior of porous ceramics for gas cleaning. *Journal of the American Ceramic Society* 87 (5), 906-913.

Launey, M.E., Munch, E., Alsem, D.H., Barth, H.B., Saiz, E., Tomsia, A.P. & Ritchie, R.O. (2009). Designing highly toughened hybrid composites through nature-inspired hierarchical complexity. *Acta Materialia* 57 (10), 2919-2932.

Liu, G. (2011) *Fabrication of porous ceramics and composites by a novel freeze casting process.* Ph.D. thesis, School of metallurgy and materials, University of Birmingham, Birmingham, United Kingdom.

Liu, Q., Ye, F., Gao, Y., Liu, S., Yang, H. & Zhou, Z. (2014). Fabrication of a new SiC/2024Al co-continuous composite with lamellar microstructure and high mechanical properties. *Journal of Alloys and Compounds* 585, 146-153.

Malshe, A., Rajurkar, K., Samant, A., Hansen, H.N., Bapat, S. & Jiang, W. (2013). Bio-inspired functional surfaces for advanced applications. *CIRP Annals-Manufacturing Technology* 62 (2), 607-628.

Meyers, M.A., Lin, A.Y.M., Chen, P.Y. & Muyco, J. (2008). Mechanical strength of abalone nacre: role of the soft organic layer. *Journal of the Mechanical behavior of biomedical materials* 1 (1), 76-85.

Meyers, M.A., McKittrick, J. & Chen, P.Y. (2013). Structural biological materials: critical mechanics-materials connections. *Science* 339 (6121), 773-779.

Moritz, T. & Richter, H.J. (2007). Ice-mould freeze casting of porous ceramic components. *Journal of the European Ceramic Society* 27 (16), 4595-4601.

Munch, E., Launey, M.E., Alsem, D.H., Saiz, E., Tomsia, A.P. & Ritchie, R.O. (2008). Tough, bio-inspired hybrid materials. *Science* 322 (5907), 1516-1520.

Pham-Huu, C., Bouchy, C., Dintzer, T., Ehret, G., Estournes, C. & Ledoux, M. J. (1999). High surface area silicon carbide doped with zirconium for use as catalyst support. Preparation, characterization and catalytic application. *Applied Catalysis A: General* 180 (1), 385-397.

Pawelec, K.M., Husmann, A., Best, S.M. & Cameron, R.E. (2014). Ice-templated structures for biomedical tissue repair: From physics to final scaffolds. *Applied Physics Reviews* 1 (2), 021301.

Preiss, A., Su, B., Collins, S. & Simpson, D. (2012). Tailored graded pore structure in zirconia toughened alumina ceramics using double-side cooling freeze casting. *Journal of the European Ceramic Society* 32 (8), 1575-1583.

Rempel, A. & Worster, M. (1999). The interaction between a particle and an advancing solidification front. *Journal of Crystal Growth* 205 (3), 427-440.

Rempel, A. & Worster, M. (2001). Particle trapping at an advancing solidification front with interfacial-curvature effects. *Journal of Crystal Growth 223* (3), 420-432.

Schoof, H., Apel, J., Heschel, I. & Rau, G. (2001). Control of pore structure and size in freeze dried collagen sponges. *Journal of biomedical materials research* 58 (4), 352-357.

Shaga, A., Shen, P., Sun, C. & Jiang, Q. (2015). Lamellar-interpenetrated Al–Si–Mg/SiC composites fabricated by freeze casting and pressure less infiltration. *Materials Science and Engineering*: A, 630, 78-84.

Sinchuk, Y., Roy, S., Gibmeier, J., Piat, R., & Wanner, A. (2013). Numerical study of internal load transfer in metal/ceramic composites based on freeze-cast ceramic preforms and experimental validation. *Materials Science and Engineering*: A, 585, 10-16.

Sofie, S.W. (2007). Fabrication of Functionally Graded and Aligned Porosity in Thin Ceramic Substrates with the Novel Freeze–Tape□Casting Process. *Journal of the American Ceramic Society* 90 (7), 2024-2031.

Szepes, A., Ulrich, J., Farkas, Z., Kovács, J. & Szabó-Révész, P. (2007). Freeze-casting technique in the development of solid drug delivery systems. *Chemical Engineering and Processing: Process Intensification* 46 (3), 230-238.

Wang X.Q. & Mujumdar A.S. (2007). Heat transfer characteristics of nanofluids: a review. International Journal of Thermal Sciences 46 (1), 1-19

Waschkies, T., Oberacker, R. & Hoffmann, M. J. (2011). Investigation of structure formation during freeze-casting from very slow to very fast solidification velocities. Acta Materialia 59 (13), 5135-5145.

Yang, T.Y., Lee, J.M., Yoon, S.Y. & Park, H.C. (2010). Hydroxyapatite scaffolds processed using a TBA-based freeze-gel casting/polymer sponge technique. Journal of Materials Science: Materials in Medicine 21 (5), 1495-1502.