

Fabrication of ceramic porous structures using the freeze-casting method

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In this paper we describe the construction of an apparatus for a method of unidirectional freeze-casting of ceramic suspensions. The cooling system is based on a cascade system with Peltier modules. The compositions of the suspensions were elaborated in two different systems of the superplasticizer (dispersing agent)/binder additives. Applying the freeze-casting method, zirconium dioxide powder (stabilized with 3% at. of yttrium oxide) was used to fabricate the ceramic matrices, which were then vacuum-infiltrated with a commercially available epoxy resin EpoFix (Struers). SEM microphotographs showed that the porous ceramic materials of a layered structure had been obtained. These layers were arranged into domains of different orientations in relation to each other, while in the domains the layers were arranged in parallel to each other. A mechanism of the processes occurring during freezing the ceramic suspensions was described on the basis of the SEM images of the cross-sections of the produced samples. We observed the key-effect of the additives (superplasticizer, binder) on the microstructure of the samples. That influence can be explained by a change in the freezing mechanism or a change in the ice crystal structure in a system containing those additives.



Key words: freeze-casting, biomimetics, ceramic forming techniques

Ceramiczne struktury porowate wytwarzane metodą freeze-casting

W ramach przedstawionej pracy opisana została budowa urządzenia służącego do jednokierunkowego wymrażania zawiesin ceramicznych metodą freeze-casting. Układ chłodzenia opiera się na systemie kaskadowym, w którym wykorzystywane są moduły Peltiera. Opracowane zostały składy zawiesin w dwóch różnych układach dodatków upłynniacz/spoiwo. Metodą freeze-casting, z proszku dwutlenku cyrkonu (stabilizowanego 3% molowo tlenkiem itru) wykonane zostały matryce ceramiczne, które następnie infiltrowano próżniowo za pomocą handlowo dostępnej żywicy epoksydowej EpoFix (Struers). Mikrofotografie SEM pokazały, iż wytworzone zostały porowate materiały ceramiczne o charakterze warstwowym. Warstwy te ułożone są w domeny o różnej orientacji względem siebie. W domenach z kolei warstwy ułożone są względem siebie równolegle. Na podstawie mikrofotografii z przekroju poprzecznego wytworzonych próbek opisano mechanizm zachodzący podczas wymrażania zawiesin ceramicznych. Zaobserwowano kluczowy wpływ dodatków (upłynniacz, spoiwo) na mikrostrukturę próbek. Wpływ ten tłumaczy się zmianą mechanizmu zamarzania, lub zmianą struktury krystalicznej lodu w układzie z tymi dodatkami.

Słowa kluczowe: freeze-casting, biomimetyka, techniki formowania materiałów ceramicznych

1. Introduction

Biomimetics (bionics) is undoubtedly an important field of the present-day science. By its development, the mankind can utilize the solutions resulting from the adaptation of the organisms living on the Earth, which often surpass the ones used so far [1]. A typical example is the Velcro fabric invented by Georges de Mestral, now commonly known as a *hook-and-loop fastener*.

The knowledge of the structures created by the organisms can also be used to obtain composite materials with significantly better mechanical parameters and lower density than the materials in current use. The examples of the materials arousing interest of many research groups are: bone (specifically the cortical bone), nacre (mother of pearl) or insects' scutum [1 - 3]. These materials are characterized by a layered structure, with a biopolymer placed between lamellas of inorganic substances (e.g. hydroxyapatite in a bone or aragonite in nacre). The interest

of scientists is also focused on the materials with a rigid inorganic skeleton of a spongy character (modelled on a spongy bone or a structure of wood) [4]. All the aforementioned materials created by the organisms, although originating from the raw materials of a comparatively low strength, possess good mechanical properties, referring both to the type and the size of the structures (at the micro or submicro level). Therefore, the attempts to reproduce their structures with the use of the much more resistant special ceramics and the properly selected plastics (e.g. PMMA) seem to be justified [5].

Among the methods of preparation of porous ceramic structures, such as the additive manufacturing technique (colloquially called 3D printing) or the formation of ceramic foams (sponges) on the basis of plastic matrices, one of the most promising techniques for the fabrication of biomimetic composites described above is a freeze-casting method (forming by controlled freezing out of a suspension). In comparison with the freeze-casting method, 3D printing requires a more expensive equipment, it

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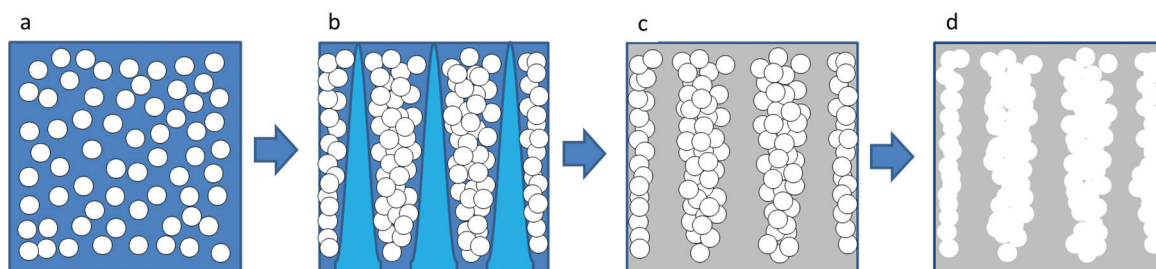


Fig. 1. A scheme of the preparation process of the ceramic structures using the freeze-casting method. A properly prepared suspension (a) is subjected to freezing out in a single direction. The ceramic grains are being pushed out of the growing ice crystals (b). The material obtained is then freeze-dried (c) and sintered, which leads to the formation of a porous ceramic structure (d).

Rys. 1. Schemat procesu otrzymywania struktur ceramicznych z wykorzystaniem metody freeze-casting. Odpowiednio przygotowana zawiesina (a) zostaje wymrożona jednokierunkowo. Ziarna ceramiczne są wypychane poza kryształy rosnącego lodu (b). Tak otrzymany materiał jest następnie liofilizowany (c) oraz spiekany, co prowadzi do utworzenia ceramicznej struktury o charakterze porowatym (d).

is more time-consuming and, above all, it does not enable reproduction of structures of a size typical for the structures found in the organisms (the manufacturers specify a minimum single layer size at the level of 25 μm , and the printing speed of 3 mm/h for such a complex element with the cross-sectional area of ca. 2 cm^2 [6]). On the other hand, foam formation leads to the structures characterized by a low mechanical strength due to the appearance of the defects in the process of a plastic matrix pyrolysis [7]. Similarly to 3D printing, foam formation enables obtaining only the systems, whose pore size significantly exceeds the size found in the biological structures. In contrast to the above cases, the freeze-casting technique is relatively inexpensive, it does not require any significant amounts of the polymer additives and, when accompanied by the adequate knowledge and experience, it makes it possible to control the structure easily by an appropriate selection of the parameters (cooling rate, solid phase content) and by the supportive substances. According to the literature reports, the structures obtained by this method are characterized by crosswise dimensions of the lamellas/pores ranging from 200 μm to even 1 μm , which demonstrates a great potential of that method in the applications to the fabrication of the biomimetic materials [7].

The freeze-casting technique is based on a controlled unidirectional freezing of a slip (an aqueous or a non-aqueous one, Fig. 1a). During the solidification, the ceramic grains are being pushed out of the crystals of the forming frozen liquid phase (Fig. 1b). The obtained product is then subjected to freeze drying, i.e. to lyophilization (Fig. 1c) in order to remove the frozen liquid phase and then it is sintered (Fig. 1d).

In the case of the aqueous slips, the solidification process leads to the formation of a layered structure, ordered in a single direction (and thus anisotropic). This procedure utilizes the phenomenon of a significant difference (by around two orders of magnitude) between the crystallization rates of water in a plane parallel with the x, y, u crystallographic axes and in a plane parallel with the z axis [8]. In the case of the ceramic slurries with a high contribution of a solid phase, some particles may also be

trapped inside the crystal, which can lead to the formation of the bridges between the successive layers [9].

As a result of the process described above, we obtain a ceramic *scaffolding* that is characterized almost exclusively by open porosity. The prepared materials can be used as the supports for catalysts, the elements of filtration systems, and after the infiltration with a plastic or a metal they can be applied as raw materials for the production of light construction materials or implants to be used in the bones (a non-infiltrated skeleton can also be used) [10]. In the case of the materials destined for such implants, the structure size and the ceramic material content in the composite may help to fit the mechanical properties so that they are as close to those of a bone as possible (especially the composite stiffness). This could lead to the reduction of the stresses occurring on a potential joint between the implant and the bone. A good example of such a material is an $\text{Al}_2\text{O}_3/\text{PMMA}$ composite with the K_{1c} value exceeding 30 $\text{MPa}\cdot\text{m}^{1/2}$ and the value of bending strength exceeding 210 MPa [11].

Apart from the control of the cooling rate or the amount of the solid phase in the suspension, other procedures are reported in the literature, concerning minor modifications of the suspension or the process itself, that have a significant effect on the structures obtained by the freeze-casting method. As a result of a template introduction (introduction of a geometrical pattern made of poly(dimethylsiloxane)) into the base of a cold finger, that can change the local temperature gradient in the system, we can obtain structures with the layers arranged in parallel with each other within the entire sample volume or forming the circles. Therefore it is possible to modify the properties of the obtained materials in various ways [12]. Using such additives as sucrose can lead to the much higher surface roughness of the ceramic layers [12]. It results in an increased adhesion of a plastic and thus in an increased rigidity of the system. Some amounts of alcohols, belonging to the other type of additives, help to adjust the pore size in the structure but at the same time to maintain the stability of other process parameters and the thickness of individual lamellas [13]. There is also a

possibility of uniaxial pressing (perpendicular to the arrangement direction of the lamellas) of the formed ceramic matrix, which makes it more compact due to the destruction of the bridges and layer cracking. Then, in the next step, the polymer is subjected to the infiltration. Because of a higher content of the inorganic substances (bricks and mortar, as reported in the literature) this structure is much more similar to the nacre, whose content reaches up to 95% vol. [11]. By utilizing the freeze-casting method it also becomes possible to obtain the non-layered structures. With the additive of gelatin, we can prepare a material of a cellular structure [9], while after adding a small amount of a zirconium acetate solution to the suspension the obtained material exhibits columnar character [8].

This paper is devoted to a description of the construction of a dedicated device for the production of porous structures by the freeze-casting method and to the presentation of the test results concerning the use of a ceramic material of zirconium dioxide stabilized with 3% at. of yttrium oxide. We decided to choose this material because of its numerous favorable mechanical properties and the fact that it is often described as having the components of the ceramic composites applied in biology (implantology).

2. Experimental

2.1 Description of the apparatus construction

Most reports, on the freeze-casting process, present the devices which utilize a system based on the chamber cooling with liquid nitrogen, coupled with the resistance heating in order to assist the proper cooling rate or to stabilize the temperature at an appropriate level.

For a more economical production process of the construction of the system we utilized the Peltier effect. For the fabrication of the system components (a freezing chamber, some structural elements of the device), we decided to apply the method of additive manufacturing FDM (Fused Deposition Modeling), commonly known as 3D printing. All the elements obtained by FDM were made of polylactide (PLA). The presented apparatus is based on a cascade cooling system in order to increase the lower limit of its temperature operating range. We used a two-channel PID controller to operate with two stages of the cooling system, and with the thermoelectric modules for the heat removal. A DC power supply was matched to each stage. As the last stage of the system a cooler supplied by a chiller (PolyScience) was used, with a mixture of water and ethylene glycol as the cooling medium. The aluminum blocks were present between the consecutive stages, serving as heat conductors from the modules to the lower stages of the cooling system. The thickness

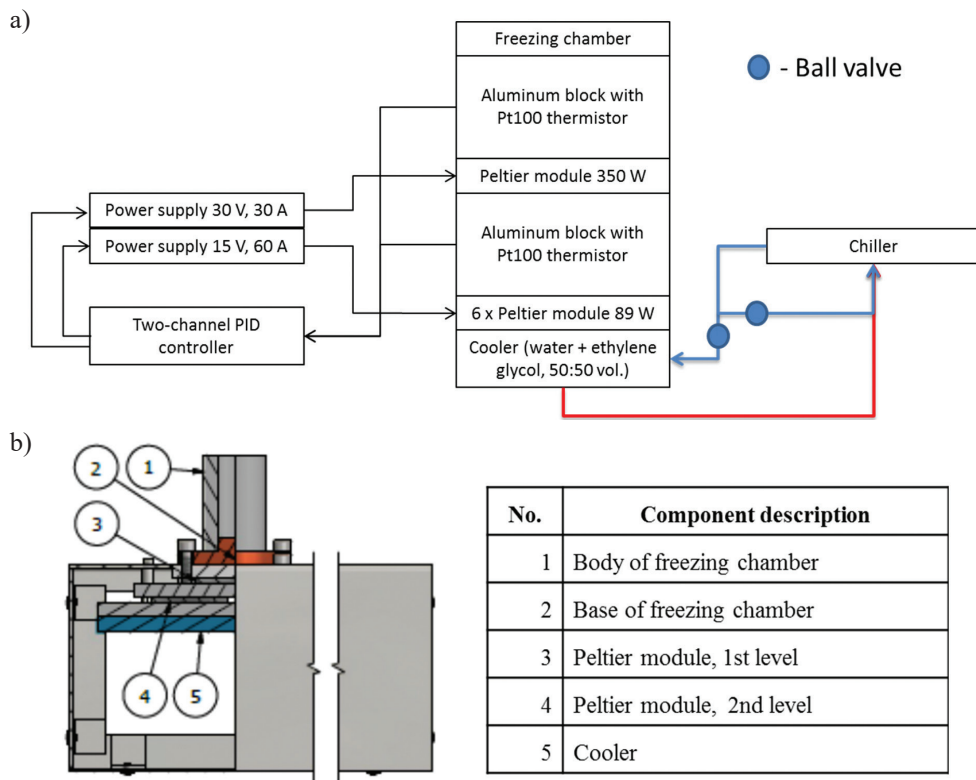


Fig. 2. A scheme (a) and a pictorial figure (b) of the constructed apparatus. Chamber size: $\varnothing = 20$ mm, $h = 30$ mm.

Rys. 2. Schemat (a) oraz poglądowy rysunek (b) zbudowanego urządzenia. Rozmiar komory wynosi: $\varnothing = 20$ mm, $h = 30$ mm.

was properly selected so as to both minimize the system inertia and to allow the thermistors to be mounted inside the blocks, which were providing the controller with the data on the temperature at each stage of the system. The scheme of the apparatus is shown in Fig. 2.

2.1. Methodology of the infiltrated ceramic preform fabrication

The initial raw materials used for the preparation of the suspensions were:

1. Tetragonal zirconium dioxide stabilized with 3% at. of yttrium oxide (CY3Z type, ZirPro Saint Gobain) with an average grain size of 0.2 μm and a specific surface area of ca. 15 m^2/g ;
2. A binder (trade name: Duramax B1000), provided by The Dow Chemical Company;
3. Deionized water;
4. An aqueous 25% solution of tetramethylammonium hydroxide (TMAH), supplied by Merck,

The procedure of the preparation of the materials:

- 1) placing the weighted samples of CY3Z and water (so as to obtain 50 ml of a suspension with 10%, 20%, 30% and 40% by volume of CY3Z) in a planetary mill (Pulverisette 6, Fritsch). Ball milling for 15 minutes at a rotational speed 250 rpm;
- 2) addition of a fixed amount of tetramethylammonium hydroxide (this amount was determined experimentally to reach the pH value of ca. 10.8 for each suspension) and ball milling again for 15 minutes at 250 rpm; This pH value results from the literature reports concerning the value of electrokinetic potential in the suspended ceramic powders [14] and the necessity of the adaptation of the medium to the binder used.

- 3) addition of a Duramax B-1000 binder in the amount of 4% by weight with respect to the content of CY3Z, followed by ball milling for 4 hours at 100 rpm;
- 4) a control measurement of pH;
- 5) suspension degassing under reduced pressure;
- 6) unidirectional freezing at a speed of 2°C/min;
- 7) freeze drying of the obtained sample in a LYO GT 2 lyophilizing cabinet (SRK-Systemtechnik);
- 8) burning out the organic additives (temperature rise at the rate of 0.5°C/min up to 800°C, holding time 1 h);
- 9) sintering (temperature rise at the rate of 3°C/min to 1480°C, holding time 2 h);
- 10) infiltration of the obtained matrix using an EpoFix epoxy resin (Struers).

In order to examine the nature of the produced materials, the prepared composites were subsequently cut in two planes: parallel and perpendicular to the direction of the layer growth, and then they were ground and polished. Such prepared microsections were subjected to the microstructure tests using an AURIGA CrossBeam Workstation (Carl Zeiss) scanning electron microscope (SEM).

3. Results

Figs. 3 and 4 show the examples of the SEM micrographs of the composites cut perpendicular to the direction of the layer growth.

The formation of ceramic layers and a polymer completely filling the space followed lyophilization, which indicates the effective matrix infiltration with plastic. Another observation concerns the formation of *domains*, with the layers inside arranged in parallel to each other,

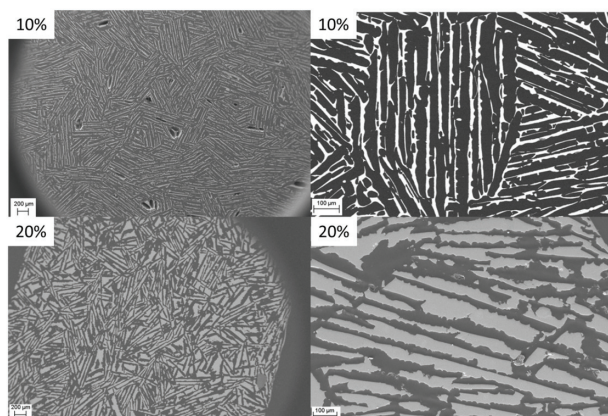


Fig. 3. SEM microphotographs taken for the samples obtained from the suspensions with 10% and 20% vol. of CY3Z, cut perpendicular to the direction of the layer growth.

Rys. 3. Mikrofotografie próbek wykonanych z zawiesin 10% i 20% obj. CY3Z zarejestrowane w kierunku prostopadłym do kierunku wzrostu warstw.

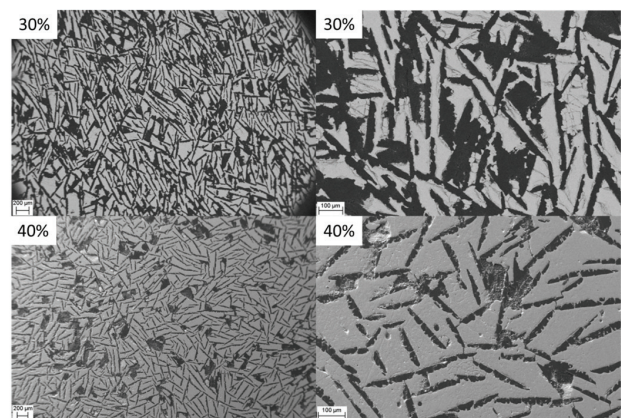


Fig. 4. SEM microphotographs taken for the samples obtained from the suspensions with 30% and 40% vol. of CY3Z, cut perpendicular to the direction of the layer growth.

Rys. 4. Mikrofotografie zarejestrowane dla próbek wykonanych z zawiesin 30% i 40% obj. CY3Z w kierunku prostopadłym do kierunku wzrostu warstw.

while the domains themselves are arranged accidentally. Most possibly, it can be explained by a simultaneous formation of many nuclei of water crystallization, each of them having a different spatial orientation. With the increase in the solid phase content one can observe an increase in the thickness of the layers and a decrease in the domain size, until their disappearance in the case of a composite with the solid phase contribution of 30% by volume. This is most likely due to a reduction of the amount of water with respect to that of zirconium dioxide, which inhibits a greater growth of the individual nuclei. Large spaces occupied by the polymer and appearing in the samples with a greater amount of the solid phase may be the residues of the air bubbles present in the suspension. The most probable explanation of that behavior is that the slip cannot be degassed completely because of a significant

increase in viscosity of the system with the increasing amount of the solid phase in the sample

Below, Fig. 5 shows the SEM images of the microstructures of the composites cut in a plane to the direction of the layer growth. In all these cases, a vertical layer growth can be observed. However, some deviations which appeared as a result of this behavior, were particularly evident in the case of a 10% vol. sample. This may result from the formation of a nucleus of crystallization having different spacial orientation, possibly due to a non-uniform temperature gradient during the freezing process. Similarly to the SEM images taken perpendicular to the growth direction, we could observe an increase in the thickness of the layers with an increasing amount of the solid phase in the composite, together with the presence of some spaces filled with a polymer, formed as a result of an insufficient degassing of the suspensions. It is also noteworthy that the ceramic layers are not continuous and are composed of numerous small units.

The picture taken during the examination of the microstructure of the cross-sections of the produced composites, can illustrate the various stages of the freeze-casting process. It is presented in Fig. 6 (for a suspension containing 20% by volume of zirconium dioxide). Three zones can be distinguished in the freezing process. The first zone is a thin layer, being a result of the liquid supercooling, followed by an abrupt crystallization leading to the powder trapping in the interior of the ice. Another part concerns the intermediate stage of the liquid crystallizations into different directions, which leads to the formation of a pseudocellular structure. Only in the next step, when the temperature gradient within the suspension becomes constant, the crystallization process starts to be unidirectional, resulting in the formation of a layered structure.

In spite of the fact that our observations were consistent with other literature reports [9,11,13], the structures of the obtained materials deviated from the assumed ones. The mutual disorientation of the layers caused by an increase in the solid phase content was surprisingly

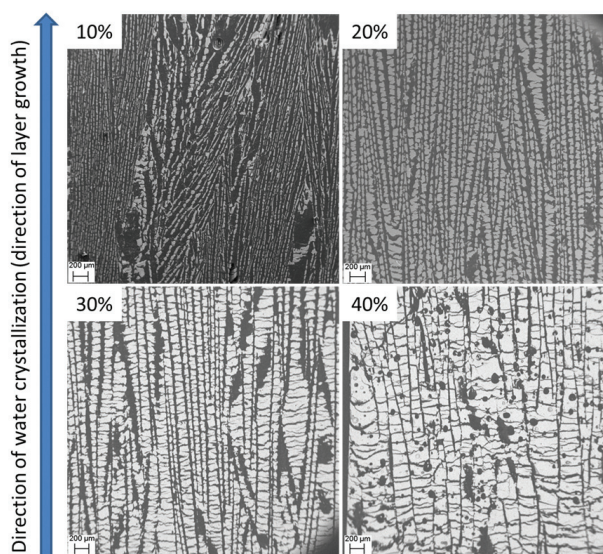


Fig. 5. SEM microphotographs of the obtained composites, taken for a microsection cut parallel to the layer growth direction.

Rys. 5. Mikrofotografie wytworzonych kompozytów zarejestrowane ze zglądu wykonanego w kierunku równoległym do kierunku wzrostu warstw.

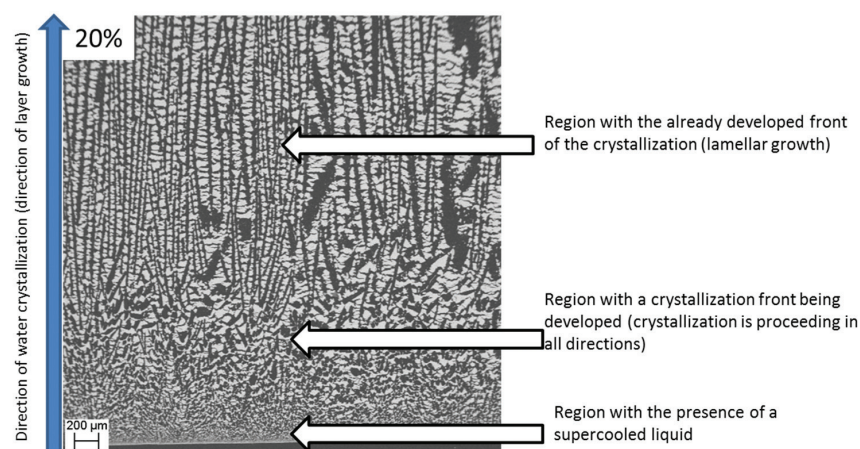


Fig. 6. An SEM microphotography showing the stages of the layer growth in the freeze-casting process.

Rys. 6. Mikrofotografia przedstawiająca etapy wzrostu warstw w procesie freeze-casting.

Tab.1. Parameters of the obtained ceramic matrices.**Tab.1.** Zestawienie parametrów otrzymanych matryc ceramicznych.

Parameters of the obtained ceramic matrices							
Sample type	10% vol. CY3Z, 4% B1000	20% vol. CY3Z, 4% B1000	30% vol. CY3Z, 4% B1000	40% vol. CY3Z, 4% B1000	10% vol. CY3Z, 1% PEG / 1% PVA / 1% Dolapix	20% vol. CY3Z, 1% PEG / 1% PVA / 1% Dolapix	30% vol. CY3Z, 1% PEG / 1% PVA / 1% Dolapix
Average layer length [μm]	298.6 \pm 119.3	290.8 \pm 171.1	368.9 \pm 154.4	-	335.6 \pm 134.5	495.2 \pm 215.8	714.6 \pm 276.6
Average layer width [μm]	12 \pm 4.2	42.7 \pm 22.6	51.0 \pm 21.5	-	9.4 \pm 3.2	22.5 \pm 5.3	34.6 \pm 9.1
Average ceramic phase content in the composite [% by volume]	24.38	47.59	55.54	69.22	24.69	48.31	56.50
Material density determined by the hydrostatic method [g/cm^3]	2.07	2.91	3.74	4.35	2.05	2.79	3.80
Material density determined by the microstructure analysis [g/cm^3]	2.32	3.47	3.85	4.52	2.34	3.51	3.91

rapid and the quality (the growth, non-uniform width and length decrease) of the layers themselves was also unexpected. Moreover, we predicted a continuity of the obtained layers (in the direction of their growth). The freeze-casting method utilizes a physical phenomenon of the solidification of the dispersion medium (i.e. water in that case). Therefore, it was noted that the differences with respect to the literature reports do not result from the properties of the applied powder but are related to the process conditions or to the additives serving as a binder and as well as the suspension pH stabilizing agent (i.e. Duramax B1000 and tetramethylammonium hydroxide, respectively). Their presence can alter: the structure of the ice being formed (in the literature there are reports on the additives causing e.g. the formation of clathrates of water and alcohols [13]), the suspension parameters (e.g. viscosity) or a decrease in the rheostability of the system (e.g. the appearance of thixotropy).

Therefore, we decided to use different substances. The following compounds were selected:

- poly(vinyl alcohol) [PVA] as a binder,
- poly(ethylene glycol) [PEG], as a plasticizer for PVA (it allowed PVA glass transition temperature to be reduced) and also as a binder,
- a commercial superplasticizer (dispersing agent) Dolapix CE64 (an ammonium salt of polymethacrylic acid, dispersed in water).

The composites were prepared according to a modified procedure:

- 1) placing the weighted samples of water and zirconium dioxide powder in a ball mill (Pulverisette 6, Fritsch). Stirring for 15 minutes at 250 rpm;
- 2) adding a dispersing agent (Dolapix), a binder (PVA) and a plasticizer (PEG). All these substances were added to the suspension in the amount of 1% by weight with respect to the solid phase content;
- 3) Stirring in a ball mill for 4 hours at a rotational speed of 100 rpm.

The further steps of the process (degassing, freezing and mechanical working) were carried out analogously to the procedure with the use of the previous dispersing agent/binder system. Fig. 7 presents the exemplary microstructures of the obtained composites (containing 10%, 20% and 30% by volume of ZrO_2).

For a comparison, on the basis of the micrographs of the composites containing both the B1000/TMAH and PEG/PVA/Dolapix additive systems, the average values of the length and width of the ceramic layers were determined in a direction perpendicular to the direction of their growth (a result based on 100 measurements, obtained using an Image J data analysis software). By the analysis of these micrographs taken both in the perpendicular and parallel directions (two images analyzed for each orientation), using a Clemex image analysis software, the contribution of the ceramic phase in the ceramic-polymer composite was determined, and then converted into density of the

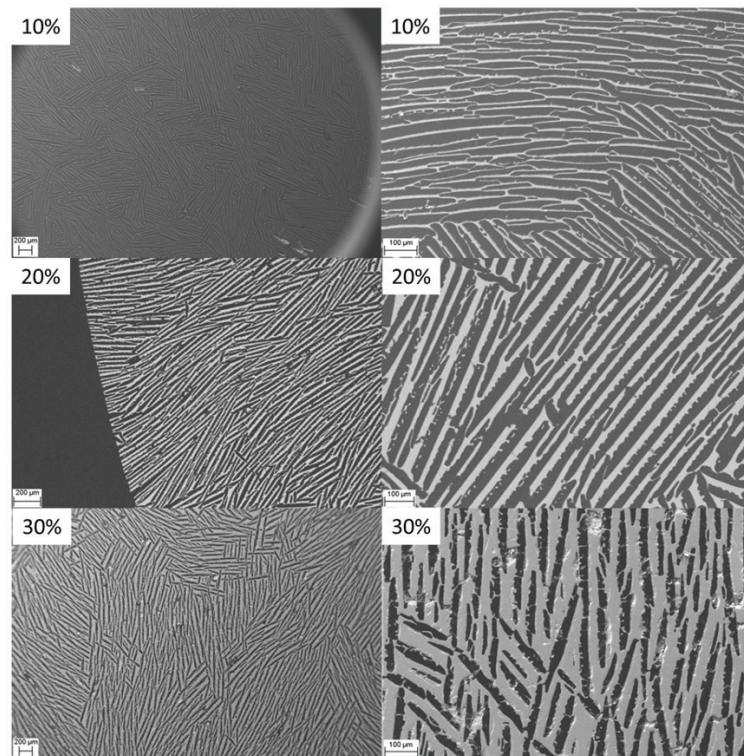


Fig. 7. SEM microphotographs of the composites based on the suspensions containing PVA, PEG and Dolapix, taken for a microsection cut perpendicular to the direction of the layer growth.

Rys. 7. Mikrofotografie kompozytów na bazie zawiesin zawierających PVA, PEG oraz Dolapix zarejestrowane ze zglądu wykonanego w kierunku prostopadłym do kierunku wzrostu warstw.

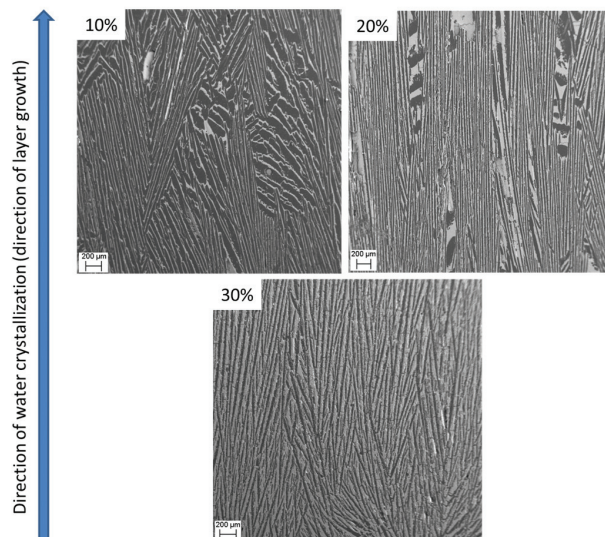


Fig. 8. SEM microphotographs of the composites based on the suspensions containing PVA, PEG and Dolapix, taken for a microsection cut parallel to the direction of the layer growth.

Rys. 8. Mikrofotografie kompozytów na bazie zawiesin zawierających PVA, PEG oraz Dolapix zarejestrowane ze zglądu wykonanego w kierunku równoległym do kierunku wzrostu warstw.

obtained materials. For a comparison, the density values of the obtained composites were also measured by the hydrostatic method. The determined parameters of the

ceramic layers and densities of the obtained composites are specified in Tab. 1.

The structures obtained from the suspensions containing the PEG/PVA/Dolapix system are characterized by a more desirable structure, i.e. by the layers of greater length, smaller width and a more regular shape (data collected in Tab. 1). Already in the case of a sample with the lowest solid phase content we could observe (i.e. 10% vol.) bridges between the layers, which were the result of trapping of small amounts of powder in the growing ice crystals. The bridge formation mechanism was also described in other reports [9, 13]. It should be noted that with an increase in the content of the solid phase the structure disorganization is not as rapid as in the case of the suspensions containing the B1000/TMAH additive system. The formation of bridges also occurs more frequently than in the case of the suspensions with a smaller solid phase content.

Moreover, some differences can be observed also in a direction parallel to the growth direction of the ice crystals. The obtained ceramic layers are continuous and are not cracked, as in the case of the samples prepared using the previous additive system.

Another fact worth observation and concerning both groups of the samples, is a larger volume fraction of the solid phase in the sintered ceramic matrix with respect to its content in the initial suspension. This fact may be explained by a phenomenon of non-uniform contraction of

the samples during the drying and sintering processes, thus resulting in a significant reduction of the distance between the ceramic layers in comparison with the contraction of the layers. The values of material density measured by the hydrostatic method are lower than the those determined via the microstructure analysis. This is probably due to the structure heterogeneity and the appearance of large pores during the freezing stage (visible in Figs. 5, 6 and 8), occurring to a much higher degree than it could be detected by SEM.

4. Conclusions

1. We constructed an apparatus that enabled us to obtain porous ceramic structures of a layered nature.
2. As a result of the vacuum infiltration process, the pores remaining after lyophilization became completely filled, as confirmed by the presented SEM photomicrographs. This indicates that a ceramic-polymer composite was fabricated.
3. SEM images of the microstructure revealed a layered nature of the samples. It was observed that a simultaneous appearance of numerous nuclei of crystallization on the chamber bottom, causes the formation of domains, with the layers inside arranged in parallel to each other. These domains are in various mutual orientations. We also noticed a significant influence of the additives used in the production of the suspension on the obtained structures. In the case of a commercial Duramax B1000 binder and tetramethylammonium hydroxide, the domains became reduced with an increasing solid phase content, until their complete disappearance. Such behavior was not observed for the PVA/ PEG/Dolapix system. This fact indicates that the additives have a key impact on the suspension parameters, which is mirrored in the nature of the obtained structures.
4. Three stages of the layer growth were observed, starting from the supercooled liquid emergence up to a development of a front of the crystallization and the layered growth of the ice crystal, which resulted directly from the process parameters.
5. The materials which were formed may be potentially applied as the supports for catalysts, the elements of filtration systems, and after their infiltration with plastic or metal they can be used as raw materials for the production of light construction materials or implants to be applied in the bones.

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