INSTITUTE OF ELECTRONIC MATERIALS TECHNOLOGY

MATERIAŁY ELEKTRONICZNE ELECTRONIC MATERIALS

QUARTERLY

Vol. 46, No. 1 - 4 2018



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WARSAW ITME 2018

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PL ISSN 0209 - 0058

A quarterly quoted on the list of scientific journals of the Ministry of Science and Higher Education 7 points - according to the statement of the Ministry of Science and Higher Education.

Published articles are indexed in databases: BazTech, CAS - Chemical Abstracts

Published articles of a scientific nature are reviewed by independent researchers.

The paper version is the primary version.

The quarterly is published in open access.

Circulation: 200 copies

Fabrication of computer generated holograms using hot embossing nano imprint lithography

Anna Rojek¹, Andrzej Kowalik¹, Jarosław Podgórski¹

The article presents the investigation to develop a technology for fabricating micro-and nanostructures of a high dimensional precision using the processes of Hot Embossing Nano Imprint Lithography. The research was carried out for three thermoplastic polymers, i.e. poly(methyl methacrylate), olefin copolymer and polycarbonate in order. The process parameters and pattern correction coefficients for shrinkage compensation have been determined. The accuracy better than 1.25×10^{-3} % has been reached for the pattern replicated onto olefin copolymer substrates.



Key words: Hot Embossing Nano Imprint Lithography, nanoimprint, computer generated holograms

Technologia wytwarzania replik hologramów syntetycznych w procesach tłoczenia na gorąco

W artykule przedstawiono technologię wytwarzania kopii (replik) mikro- i nanostruktur o dużej precyzji wymiarowej w procesach tłoczenia na gorąco (*Hot Embossing Nano Imprint Lithography*). Badania prowadzono dla trzech polimerów termoplastycznych - polimetakrylanu metylu, kopolimeru olefinowego oraz poliwęglanu. Określono warunki procesów i współczynniki korekty wzorów kompensujące skurcz towarzyszący kopiowaniu struktur. Uzyskano repliki, dla których względny błąd wymiarów poprzecznych wynosił poniżej 1,25 x 10⁻³ %.

Słowa kluczowe: tłoczenie na gorąco, nanoimprint, hologramy syntetyczne

1. Introduction

The microlithographic process based on hot embossing of thermoplastic materials (called Hot Embossing Nano Imprint Lithography - HE NIL) is an efficient and simple technology of the fabrication of 3D structures with the submicron elements. This process was classified by International Technology Roadmap for Semiconductors (ITRS, www.itrs.net) as one of the new lithographic methods referred to as Next Generation Lithography (NGL), expected to enable manufacturing structures of a size even below 32 nm. A technology with such a resolution can thus be successfully applied to produce the replicas of the structures whose fabrication requires the use of the most advanced and very expensive microlithographic methods, i.e. the electron-beam pattern generation or EUV projection printing.

HE NIL is being increasingly used for the production of micro-opto-electro-mechanical elements and systems (MOEMS). The examples can be microflow devices (Lab--on-chip) [1 - 2], micro-lenses, the structures improving brightness of the LCD screens [3] and computer-generated holograms [4].

In the HE NIL process, a pattern is transferred onto a thermoplastic polymer substrate heated to a temperature exceeding glass transition temperature (T_g) , using a master stamp with a given contact force. After cooling the stamp/substrate system to a temperature below T_g and detachment, the replicated pattern is preserved in the polymer.

However, obtaining high quality replicas, especially in the case of the large surface area microstructures (a few to several dozen cm²), requires a very careful selection of the process conditions, primarily the temperature and pressure force during embossing and the temperature of detachment. The too high value of the embossing temperature will cause large deformations of the substrate, while the too low value will result in a loss of the fidelity of the replicated relief (a relief too shallow, large distortion of small elements). Similarly, the temperature which gets too high during de-embossing may be the reason for the pattern deformation, while temperature that is too low may cause the destruction of the stamp and the substrate due to the stresses induced by the large differences in their thermal expansion coefficients [5 - 9].

A separate problem refers to the significant changes in the size of the replicas with respect to the original. The accurate thermal shrinkage compensation is particularly important in the case of synthetic holograms (computer generated diffractive optical structures, whose operation is based on the light diffraction). The dimensional accuracy of such elements should be comparable with the wavelength of the light, for which they are designed. Otherwise, it could lead to a significant deterioration of the quality of the wave front formed by the element.

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For instance, for one of the basic diffractive optical elements, i.e. a diffractive lens, the lack of proper compensation will cause a change in the focal length and aberrations, which will result in a deformation of the focus. The obtained element will be characterized not only by the altered basic parameter (focal length), but also by a much worse quality (high spherical aberration).

In this paper we report on the research oriented towards the development of the fabrication processes (part 2) and the compensation of shrinkage (part 3) in the HE NIL processes for the three most commonly used thermoplastic polymers. Part 4 presents the results of the applied solutions for fabricating COC replicas. Part 5 contains a summary of the research.

2. Manufacturing process

The investigations were carried out for the three most common types of polymer substrates, namely: poly(methyl methacrylate) - PMMA, olefin copolymer - COC and polycarbonate - PC. For the replicating processes we used the HE NIL EVG510 nanoimprint system. That device enables replicas on the substrates of a diameter up to 100 mm. The embossing process takes place in the vacuum chamber (pressure ≤ 2 mbar), which prevents air trapping in the relief being produced. The maximum pressure force is 10 kN and it is controlled with an accuracy of \pm 3%. The system allows the independent control of the heating of the substrate and the stamp for the temperature up to 550°C (heaters and temperature sensors placed in the base and in the piston; the control with an accuracy of $\pm 2\%$). A single-sided cooling system located in the base was used to controll cooling of the bottom plate. In the HE NIL processes a soft stamp was used, i.e. a stamp with a relief made in a polymer layer (a Fluorolink MD700 photopolymer, thickness 150 - 250 µm), applied onto a glass

substrate. A stamp like this, especially in the case of the structures with a large surface area, has two important advantages, namely:

1) it provides much better contact with the substrate than hard stamps (micro-waviness smoothing),

2) it makes the detachment process of replica from the stamp easier.

For the fabrication of a soft stamp we used a master stamp made in a process of electron-beam lithography (Vistec SB251), that guaranteed the accuracy of the position of the pattern elements at the level of 10 nm.

For each of the selected polymers, technological tests were carried out, in which the values of contact force were changed in the range of 5 - 8 kN, the temperature during embossing was in the range 15 - 25°C above T_g , and temperature during separation was in the range 5 - 15°C below T_g .

The maximum possible heating rate of the system was assumed as 10° /min, and a much lower cooling rate of 2° /min, which allowed precise control of the temperature distribution of the stamp-substrate system prior to the separation process and thus ensured high process reproducibility. The parameters of the processes that were considered optimal, based on inspection of replicas using the optical and electron microscopes, are presented in Tab. 1.

Fig.1 shows the replicas of the eight- and fourphase-level diffractive lenses as the examples of the structures made on the basis of the optimized process. The examination of their optical properties revealed that the replicas do not deviate in quality from the originals, with the diffraction efficiency of the replicated lenses equal to 0.99 ± 0.01 with respect to the originals in the case of the eight-level profiles, and to 1.00 ± 0.01 in the case of the four-level profiles (the measured efficiency differences were within the margin of the measurement error).

Tab. 1. The parameters of the HE NIL processes for the selected polymer substrates. **Tab. 1.** Parametry procesów HE NIL dla wybranych podłoży polimerowych.

	replica material			
	process parameters	PMMA	COC	PC
	heating rate [ºC/min]	10	10	10
	temperature [ºC]	125	150	170
copying	contact force [N]	7000	7000	7000
	contact time [min]	1	1	1
concretion	cooling rate [ºC/min]	2	2	2
separation	temperature [ºC]	90	120	138



Fig. 1. Images of the central part of the four- and eight -phase-level diffractive lenses (top and bottom, respectively) (Veeco Contour GTK 1 optical profilometer): on the left – a quartz original, on the right – a replica on COC substrate.
Rys. 1. Obrazy soczewek dyfrakcyjnych o czterech (u góry) i ośmiu (u dołu) poziomach fazowych (profilometr optyczny Veeco Contour GTK 1): z lewej – oryginał kwarcowy, z prawej – repliki na podłożu COC.

3. Shrinkage compensation

High temperatures of the copying process $(120^{\circ} - 170^{\circ}C)$ and large differences between the values of thermal expansion coefficient of the materials of the stamp (glass, 3×10^{-6}) and the replica (polymer, $60 \times 10^{-6} - 70 \times 10^{-6}$) result in the dimensions of the copied structures being significantly different from the dimensions of the stamp. However, provided that we know the shrinkage accompanying the copying process, we can eliminate these errors by fabricating a stamp with a properly enlarged pattern. Taking into account the fundamental dependence:

$$\delta = c \ge \Delta T, \tag{1}$$

where δ - shrinkage, *c* - linear expansion coefficient, ΔT - temperature difference, the theoretical value of the replica shrinkage can be determined on the basis of the thermal expansion coefficients of the materials of the substrate c_R , and the stamp c_S , using the dependence:

$$\delta_{\text{Reoret}} = c_{\text{R}} \left(T_{\text{g}} - T_{0} \right) \left[1 + c_{\text{S}} \left(T_{\text{g}} - T_{0} \right) \right], \tag{2}$$

where: $T_{\rm g}$ – glass transition temperature, assumed as the temperature value during replication, $T_{\rm 0}$ - ambient temperature, $c_{\rm s}$ ($T_{\rm g} - T_{\rm 0}$) – a term expressing the change in the dimension of the stamp at the embossing temperature.

However, if we take into account that the transition

temperature of a polymer from a plastic state to a fully elastic state is not clearly defined (it is rather a certain range within the glass transition temperature range, T_g), it can be assumed from the outset that the theoretical method will be erroneous. We decided that the experimental determination of the shrinkage, and the shrinkage-based determination of the correction factors necessary for the shrinkage compensation, should provide much more accurate dimensions of the replicas.

The measurements were taken for each of the tested materials for two replicas with a test pattern of 50 x 50 mm², consisting of an array of 5 x 5 markers that were placed every 10 mm. The measurements were done using electron-beam lithography system Vistec SB251. The system allows for the use of an electron beam to scan a selected area of the substrate (similarly to an electron scanning microscope) and to determine the position of the selected topological element (a marker) with an accuracy up to 10 nm. In practice, due to the scanning limitations of the polymer substrate (charging effects, polymer destruction due to the exposition of a high energy beam), the accuracy of the method is much lower, at the level of 0.5 µm. However, such an accuracy can be considered sufficient, because the relative error of the shrinkage measurement would be 5 x 10^{-5} and 1 x 10^{-5} regarding a distance between the adjacent markers and the most distant markers, respectively.

The shrinkage values, determined experimentally, are shown in Tab. 2.

Tab.	2.	The results of the shrinkage measurements.	
Tab.	2.	Wyniki pomiarów skurczu replik polimerowych.	

	stamp material	replica material			
	glass	PMMA	COC	PC	
thermal expansion coefficient [x10 ⁻⁵ /K]	0.325	6.5	6.0	7.0	
$T_{g}[^{0}C]$	-	100	130	150	
$T_{\rm o}[^{\rm o}{\rm C}]$	22	22	22	22	
theoretical shrinkage δ_{Rteoret} [x10 ⁻³]	-	6.36	8.75	12.69	
measured shrinkage $\delta_{\rm R}$ [x10 ⁻³]	-	6.06 ± 0.04	6.43 ± 0.03	8.31 ± 0.06	
pattern correction factor	-	1.00610	1.00647	1.00838	

The linear contraction of the replica, δ_{p} , was determined as a change in dimension Δl with respect to the values of nominal distance $l_0: l_0: \delta_R = \Delta l / l_0$. The value present in the table for a given substrate corresponds to an average of all the measurements on both replicas. A theoretical shrinkage value, determined from the aforementioned dependence (2), is also shown in the table.

A comparison between the both shrinkage values (i.e. the theoretical and measured one) confirms the thesis that the theoretically calculated shrinkage cannot be the basis for the determination of the pattern dimensional correction factor for the stamp and thus justifies the experimental procedure of the shrinkage determination for the specific conditions of the HE NIL process.

4. Experimental verification of shrinkage compensation

The evaluation of the dimensional accuracy of the replicas, for which the correction factors were applied at the design stage, was carried out for COC substrates. The master stamp with the test pattern with an area of 50 x 50 mm², corrected in the scale 1.00647: 1, was made in the electron-beam lithography process (SB251 system). During the fabrication of the replicas, the previously determined parameters of the HE NIL process were applied (Tab. 1 - contact force 7 kN, embossing temperature 150°C, de-embossing temperature 120°C). The results of the measurements of the replica are presented in Tab. 3.

The mean values for both measured distances are in

Tab. 3. Wyniki pomiarów repliki wykonanej na podłożu COC.

Tab. 3. The results of the COC replica measurements

a very good agreement with the nominal values. The errors are within 0.5 µm, which means a relative error even below 10⁻⁵ with respect to the distance of 50 mm. The replicas fabricated with such an accuracy can be treated as fully equivalent to the originals manufactured in the much more complicated and time-consuming, and therefore also more expensive electron-beam lithography processes. The HE NIL technology can be used as a much cheaper method of the production of the high-quality computer generated holograms.

5. Summary

The investigations were carried out in order to develop an effective technology for the production of the micro- and nanostructures replicas with high dimensional accuracy, using the processes of hot embossing nano imprint lithography (HE NIL). We examinated three types of the most commonly used thermoplastic polymers, i.e. poly(methyl methacrylate), olefin copolymer and polycarbonate. For the decided parameters of the HE NIL processes, the coefficients of the shrinkage compensation were determined experimentally. The effectiveness of the compensation was verified for the processes performed on COC substrates. Because of the implementation of the dimensional correction of the stamp, we could obtain the replicas with the relative errors below 1.25×10^{-5} . Such a high accuracy demonstrates not only a very high effectiveness of the shrinkage compensation, but also a very good repeatability of the proposed processes.

	measurement results				
nominal distance [µm]	mean value [µm]	deviation [µm]	relative error x10 ⁻⁵		
25 000	25 000.31	± 0.37	1.24		
50 000	50 000.43	± 0.49	0.87		

The developed technologies, by ensuring the production of the replicas with a quality equivalent to the originals manufactured in much more complex electron-beam lithography processes, can be successfully applied for fabricating of holograms ensuring a very high quality of the wave front.

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Covering glass microspheres with Al₂O₃ or AlN by low-temperature atomic layer deposition

Rafał Stankiewicz¹, Anna Piątkowska¹

Thin layers of Al_2O_3 and AIN were deposited on the surface of borosilicate glass microspheres in an ALD reactor at 50 and 150°C, respectively. They were imaged by SEM microscopy. X-ray EDS spectroscopy was used to assess chemical composition but it was also the basis for a thickness determination method. Al_2O_3 layers between 20 and 100 nm were obtained, with a constant growth rate of 1.2 Å per deposition cycle. AIN formed continuous but always very thin films on the spheres, generally 5 to 10 nm, even if it was growing much thicker on control glass slides, at 0.8 Å per cycle.



Key words: ALD, EDS, dielectric layers, glass microspheres

Pokrywanie mikrosfer szklanych Al₂O₃ lub AlN metodą niskotemperaturowego osadzania warstw atomowych

W reaktorze ALD osadzano cienkie warstwy Al_2O_3 i AlN na mikrosferach ze szkła borokrzemowego w temperaturach odpowiednio 50 i 150°C. Obrazowano je przy pomocy skaningowego mikroskopu elektronowego. Spektroskopia rentgenowska EDS była wykorzystywana do badania składu chemicznego, ale stanowiła także podstawę dla metody wyznaczania grubości warstw. Otrzymano warstwy Al_2O_3 o grubościach od 20 do 100 nm przy stałej szybkości wzrostu 1,2 Å/cykl. AlN tworzył natomiast ciągłe, lecz zawsze bardzo cienkie warstwy (zwykle 5 do 10 nm), mimo że na kontrolnych płytkach szklanych uzyskiwano znacznie większe grubości, a szybkość wzrostu wynosiła 0,8 Å/cykl.

Słowa kluczowe: ALD, EDS, warstwy dielektryczne, mikrosfery szklane

1. Introduction

Micro-scaled glass spheres or beads are an industrially made product with numerous applications [1]. They can serve as a filler in chemicals, paper [2] and synthetic materials [3] or as a spacer in adhesives [4]. They can also be used for shot peening of various surfaces. When incorporated in paints, coatings and mortar, they improve durability, provide thermal insulation and enhance the surface aspect [5 - 8]. In such substances, spheres can diffuse, refract or reflect light, the latter being particularly important for road marking paints [9]. The optical or decorative effect can be modified by employing glass microspheres coated with thin layers of other materials.

Oxide-coated beads are used in a number of unrelated applications. For instance, layers of SnO_2 and TiO_2 are photocatalysts [10], the latter being used for water decontamination [11, 12]. PbO₂ can serve as an additive for lead acid batteries [13], while CoFe_2O_4 has interesting magnetic properties [14] and is also a strong microwave absorber [15]. Such layers are deposited on the spheres by different chemical methods, such as the sol-gel method [10, 12], electroless deposition [13], the coprecipitation method [14 - 15] or chemical vapor deposition [11].

Atomic layer deposition (ALD) is a penetrating and self-limiting deposition technique, appropriate for ob-

taining thin uniform layers of chemical compounds on arbitrarily shaped surfaces. It is widely employed to deposit dielectric layers in the fabrication of semiconductor devices. Among the materials commonly deposited by ALD, aluminum oxide (Al₂O₃) is used, for example, as the gate oxide in field-effect transistors and aluminum nitride (AlN) can be used in piezoelectric devices or as a passivation layer. Both materials can also serve as antireflective layers. Typically, substrate temperatures of the order of 300°C are used for their deposition. It is possible, however, to adapt such processes to much lower temperatures [16], which extends the range of possible substrate materials (e.g. to glass). In the present work, we investigated if a controlled and uniform deposition can still be achieved if flat substrates are replaced with a pile of glass microspheres.

2. Experimental

Dielectric layers were deposited on borosilicate glass spheres, with different diameters present in each sample, ranging from a few micrometers to over 200 μ m (Fig. 1), but mostly comprised between 20 and 150 μ m. Visually, the spheres were forming a fine white powder. Their wall

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Fig. 1. Glass microspheres imaged by scanning electron microscopy. The diameters of selected spheres were measured. **Rys. 1.** Obraz mikrosfer szklanych ze skaningowego mikroskopu elektronowego (SEM). Zmierzono średnice wybranych sfer.

thickness was of the order of 1 μ m. As the spheres were hollow, they could be easily damaged while handling and, consequently, many fragments of other spheres were present on their surfaces (Fig. 2).

All the deposition processes were conducted in a Picosun R200 Advanced ALD reactor. Trimethylaluminium [TMA, $(CH_3)_3A$] was used as the Al precursor and nitrogen was the carrier gas. Aluminium oxide (Al_2O_3) was deposited by a thermal process with deionized water vapor employed as the oxygen precursor. In a different process, N_2 gas was flowing to the reactor chamber through a remote, inductively coupled RF plasma generator, where it was excited at ca. 2 MHz. This configuration should deliver a high concentration of charge-neutral plasma species to the substrate, allowing the deposition of aluminium nitride (AlN) layers. Alternate precursor pulses were always separated by flushing of the system with the carrier gas, argon being used to flush the plasma line.

An amount of approximately 200 mg of glass spheres was evenly spread over a 33 mm circular area of the reactor chuck, forming a ca. 2 mm thick powder-like layer with a surface density of the order of 20 mg/cm². The microspheres were placed in the reactor along with microscope slides (soda-lime glass). As the latter had a plane surface, they could be examined with a spectroscopic ellipsometer (Horiba UVISEL 2).

Both the spheres and the slides were imaged after deposition with a Carl Zeiss AURIGA CrossBeam Workstation scanning electron microscope (SEM). The spheres had to be glued on a carbon tape and covered with a thin layer of Au-Pd in order to reduce electrical charge accumulation. The glass slides were fractured to measure the thickness of the deposited layer.

The energy-dispersive X-ray spectroscopy (EDS) system of the SEM was used to analyze the chemical composition of the deposited layers but it was also employed to determine their thickness. This method requires a numerical model describing the interactions of electrons



Fig. 2. SEM image of a single glass microsphere. Small fragments of other (broken) spheres can be seen on its surface.Rys. 2. Obraz SEM pojedynczej mikrosfery szklanej. Na powierzchni widać niewielkie fragmenty innych, uszkodzonych sfer.

in the solid material. The model must take into account the mass density of the layer and substrate, the expected thickness range, and the SEM accelerating voltage. Such models were elaborated by performing Monte Carlo simulations of electron trajectories (using CASINO software). The ratios between EDS signals from elements expected in the deposited layer (in this case, Al) and in the substrate (Si) were then calculated from experimental spectra and fitted to the model, which yielded a thickness estimation. The above procedure was previously tested to give results consistent with spectral ellipsometry, notably for thin layers of Al_2O_3 on Si. A similar method is used in the ThinFilmID system, developed by Oxford Instruments [17].

3. Results and discussion

3.1. Aluminium oxide

After a series of preliminary ALD processes on Si and glass substrates, a temperature of 50°C was chosen, which was safe for the glass, high enough to be stabilized by the reactor heaters and resulted in an uniform Al_2O_3 deposition (Fig. 3). EDS mapping had confirmed that both deposited elements were present across the glass surface (Fig. 4). On both substrates, the refractive index of the oxide layer, determined by ellipsometry, had an average value of 1.57 at 633 nm wavelength. Deposition on the glass microspheres was therefore conducted at the same temperature.

After 200 cycles, the dielectric coating was not visible on a broad SEM image (Fig. 5) but a high-magnification (ca. 20 000x) micrograph of a broken sphere showed clearly the edge of the Al_2O_3 layer (Fig. 6). Many isolated low-profile objects, with a chemical composition similar to the deposited layer, were observed on the spheres sur-



Fig. 3. SEM measurement of the Al_2O_3 layer on a fractured microscope slide after 200 deposition cycles. The imaging angle may cause a slight underestimation of the thickness.

Rys. 3. Pomiar SEM warstwy Al₂O₃ na przełomie płytki mikroskopowej po 200 cyklach osadzania. Kąt obrazowania może powodować lekkie zaniżenie grubości.



Fig. 4. Map of the summed intensity of EDS signals from Al and O after 400 deposition cycles. The upper part of the image corresponds to the oxide-covered surface of the microscope slide. The bottom part shows the glass fracture.

Rys. 4. Mapa rozkładu intensywności zsumowanego sygnału EDS pochodzącego od pierwiastków Al i O po 400 cyklach osadzania. U góry znajduje się powierzchnia płytki mikroskopowej pokryta warstwą tlenku, a niżej – przełom szkła.



Fig. 5. Microspheres after depositing a 23 nm layer of Al_2O_3 . Despite being covered with a thin conductive layer (Au-Pd), the spheres accumulate some electric charge, which results in apparent shadows on the SEM image.

Rys. 5. Mikrosfery po osadzeniu 23 nm warstwy Al₂O₃, Pomimo pokrycia cienką warstwą przewodzącą (Au-Pd), sfery gromadzą ładunek elektryczny z wiązki elektronów, co objawia się cieniami na obrazie SEM.

face (Fig. 7). The absence of such objects on uncoated spheres, as well as their geometry, indicates these are Al_2O_3 crystallites.

In order to obtain layers of different thicknesses, the number of ALD cycles was varied between 175 and 800 cycles, which corresponds to deposition times from 90 minutes to nearly 7 hours. The layers deposited on glass slides were measured with ellipsometry, SEM imaging and EDS analysis. In one case, a crater with vertical walls (Fig. 8) was etched in the glass with a focused ion beam (FIB). The vertical section thus obtained appeared difficult to image because of strong electric charging from



Fig. 6. Al_2O_3 layer visible on the surface of a broken sphere. The spots on the surface were identified as damage caused by the microscope electron beam, as they were appearing progressively with successive scans.

Rys. 6. Warstwa Al₂O₃ widoczna na powierzchni pękniętej sfery. Kropki na powierzchni zidentyfikowano jako uszkodzenia wywołane przez wiązkę elektronów mikroskopu, ponieważ pojawiały się stopniowo przy kolejnych skanowaniach.

the SEM electron beam, which led to unsharp micrographs at higher magnifications. Additionally, the FIB etching itself had caused some blurring of the materials interface. Consequently, the measured Al_2O_3 thickness ranged from 85 to 120 nm but we assume that the measurement shown in Figure 9, close to 90 nm, is the most accurate. Direct measurements on the spheres were performed by analysis of EDS signal collected from a delimited area on the top of an individual sphere (Fig. 10). The thickness values thus obtained from 8 to 10 random spheres from one sample were then averaged (Fig. 11).

It appeared that 20 to 100 nm of dielectric was de-

posited in one process. The dependence between process length and Al_2O_3 thickness is shown in Fig. 12. It can be seen that the different measurement methods gave similar results but those obtained from the spheres (blue circles) are slightly higher and more linear with a growth rate of 1.2 Å per cycle.



Fig. 7. An example of low-profile crystallite observed on a sphere surface after 175 Al₂O₃ deposition cycles.

Rys. 7. Przykład krystalitu o niewielkiej wysokości widocznego na powierzchni sfery po 175 cyklach osadzania Al_2O_3 .

T

1 µm

91.37 nm



Fig. 8. A trapeziform FIB crater with vertical walls in a glass slide with an Al_2O_3 layer (800 deposition cycles). Prior to the ion etching, the sample had been covered with Au-Pd and, locally, also with platinum in order to avoid electrical charge accumulation and to protect the surface.

Rys. 8. Trapezowy krater z pionową powierzchnią w głąb materiału wytworzony poprzez trawienie jonowe (FIB) w płytce szklanej z warstwą Al₂O₃ (800 cykli osadzania). Przed trawieniem próbkę pokryto warstwą Au-Pd, a miejscowo także platyną, aby uniknąć gromadzenia się ładunku elektrycznego i zabezpieczyć powierzchnię.





Fig. 10. a) SEM image of one of the microspheres chosen for thickness measurement after 200 cycles of Al_2O_3 deposition. The rectangular measurement area is indicated. b) Map of the intensity of EDS signal from Al measured in the same area. The average layer thickness determined for this sphere was 23.8 nm.

Rys. 10. a) Obraz SEM sfery wybranej do pomiaru grubości po 200 cyklach osadzania Al₂O₃, Zaznaczono prostokątny obszar pomiarowy. b) Mapa natężenia sygnału EDS od pierwiastka Al w tym samym obszarze. Dla tej sfery wyznaczono średnią grubość warstwy 23,8 nm.



Fig. 11. SEM image with indicated diameters of random microspheres chosen for EDS thickness measurement after 175 Al_2O_3 deposition cycles. For spheres 1 to 8, the results of these measurements were, respectively: 28.5, 23.8, 23.0, 25.0, 24.7, 22.9, 25.9 and 19.0 nm. As the individual spheres undergo random rotations between oxide deposition and measurement, it can be assumed that the entire surface of each sphere was covered.

Rys. 11. Obraz z SEM z zaznaczonymi średnicami ośmiu przypadkowych mikrosfer wybranych do pomiaru grubości metodą EDS po 175 cyklach osadzania Al₂O₃. Dla sfer nr 1 do 8 pomiary te dały odpowiednio wyniki: 28,5; 23,8; 23,0; 25,0; 24,7; 22,9; 25,9 i 19,0 nm. Ponieważ poszczególne sfery ulegają przypadkowemu obróceniu w czasie między osadzaniem tlenku a pomiarem, można przyjąć, że została pokryta cała powierzchnia każdej z nich.



Fig. 13. SEM image of a glass slide with a 14 nm AlN layer after 177 deposition cycles. The surface has good uniformity with small (~10 nm) crystallites.

Rys. 13. Obraz SEM płytki szklanej z warstwą AlN o grubości 14 nm po 177 cyklach osadzania. Powierzchnia o dobrej jednorodności, z niewielkimi (~10 nm) krystalitami.

3.2. Aluminium nitride

In Ref. [18], a deposition temperature above 140°C and a H_2/N_2 plasma exposure time of at least 25 s were necessary to avoid the oxidation of AlN films after unloading from the ALD reactor. Similarly, in our study, an initial comparison of layers obtained at 100 and 150°C with pure N_2 plasma exposure times of 10 and 30 s showed that only



Fig. 12. Thicknesses of aluminium oxide obtained during five ALD processes at 50°C as a function of the process length. The SEM measurements were realized on the fractured surface of a glass slide for the 200-cycle process and on a FIB-etched section of a glass slide for the 800-cycle process. In both cases, the full range of the obtained values is shown along with their average. **Rys. 12.** Grubości tlenku glinu uzyskane podczas pięciu procesów ALD w temperaturze 50°C w funkcji długości procesu. Pomiar

SEM wykonano na przełomie płytki szklanej dla procesu o długości 200 cykli i na przekroju FIB płytki szklanej dla procesu o długości 800 cykli. W obu przypadkach zaznaczono wartość średnią i rozrzut otrzymanych wartości.



Fig. 14. Thicknesses of aluminium nitride obtained during four ALD processes, all of which were conducted at 150°C. The vertical bars show the full range of the observed values.

Rys. 14. Grubości azotku glinu uzyskane podczas czterech procesów ALD. Wszystkie wykonywano w temperaturze 150°C. Słupki pokazują zaobserwowany rozrzut grubości.

the AlN deposited at the higher temperature and with the longer exposure time had a correct refractive index (1.8), a deposition rate of more than 0.8 Å per cycle and a good layer uniformity (Fig. 13). Subsequent processes were hence conducted using these parameters.

Fig. 14 shows the AlN layer thickness as a function of process length for processes from 145 to 625 cycles.

The use of plasma resulted in longer deposition cycles than for Al_2O_3 , therefore these processes were taking up to 9.5 hours.

For glass slides, the energy selective backscattered (EsB) electron detector of the SEM microscope was useful for discerning the AlN layer from the fractured glass



Fig. 15. Imaging with the mass contrast EsB detector shows that the AlN layer on a glass slide is ca. 100 nm-thick after 625 deposition cycles.

Rys. 15. Obrazowanie detektorem kontrastu masowego EsB wskazuje, że warstwa AlN na płytce szklanej ma grubość około 100 nm po 625 cyklach osadzania. (Fig. 15). A wide range of thicknesses, from 14 to 110 nm, was obtained, with the average deposition rate reaching 1.8 Å per cycle at 625 cycles. On microspheres, however, the dielectric layer appeared to be very thin independently of the number of cycles. The EDS spectra were very different in both cases (Fig. 16) and the analysis showed that there is only 5 to 10 nm of AlN on most spheres.

It is known that AlN growth by chemical methods is highly sensitive to the presence of moisture, which should be eliminated from the reactor [19]. Nevertheless, a glass surface which is exposed to atmospheric air for an extended time will progressively adsorb water. A complete dehydration, i.e. removal of the physically adsorbed H_2O molecules, leaving only chemisorbed OH groups, occurs after heating to about 200°C [20], which exceeds our deposition temperature. The glass slides used in our experiment were subjected, shortly before deposition, to a cleaning procedure involving the use of acetone; however, no pretreatment was applied to the powder-like spheres. This leads us to assume that the limited growth observed on the latter substrates was caused by water or impurities present on their surface.

Groups of crystallites and irregular shapes were observed on the surface of all spheres. They were more numerous on spheres where the AlN thickness was lower than the average by EDS analysis (Fig. 17). Nevertheless, imaging with the EsB detector did not show any variations



Fig. 16. EDS spectra obtained for the same deposition process and with the same measurement parameters (accelerating voltage 4 kV) a) from a glass slide. The absence of a peak from Si (contained in the glass) indicates it was suppressed by a thick AlN layer. (This peak can still be observed with different measurement parameters, which allows thickness calculation). b) from the surface of a sphere. The Si peak is very strong compared with the Al one, which indicates a very thin AlN layer.

Rys. 16. Widma EDS uzyskane dla tego samego procesu i tych samych parametrów pomiaru (napięcie przyspieszające 4 kV) a) z płytki szklanej. Brak widocznego piku od Si (zawartego w szkle) wskazuje na jego stłumienie przez grubą warstwę AlN. (Pik ten można jednak ujawnić przy innych parametrach pomiaru, co pozwala na obliczenie grubości). b) z powierzchni sfery. Pik Si jest bardzo silny w porównaniu z Al, co wskazuje na bardzo cienką warstwę AlN.



Fig. 17. SEM image of a microsphere surface after deposition of an AlN layer (375 deposition cycles). The thickness given by EDS analysis is 4 nm.

Rys. 17. Obraz SEM powierzchni mikrosfery po osadzeniu warstwy AlN (375 cykli osadzania). Grubość wyznaczona metodą EDS wynosi 4 nm.

in chemical composition across the surface, which proves that the AlN layer was continuous.

4. Conclusions

Aluminium oxide was deposited on glass microspheres by ALD at 50°C using TMA and H_2O as precursors. The experiment showed that, even on substrates with a highly curved surface, an arbitrary layer thickness can be obtained with good uniformity and repeatability. Still, the deposition of aluminium nitride at 150°C from TMA and pure N_2 plasma resulted in thin continuous layers. In both cases, EDS spectroscopy could be effectively used to assess the thickness of dielectric coating on substrates which are not plane at the microscale.

Acknowledgments

The authors would like to thank Krystyna Przyborowska and Beata Stańczyk for preparation of the glass and silicon substrates used in this study. The glass microspheres were provided by NGT Technology Sp. z o.o. (Działdowo, Poland).

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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, refering 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 freezecasting 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 Al₂O₃/PMMA composite with the K_{1c} value exceeding 30 MPa \cdot 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 dedided 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: $\emptyset = 20$ mm, h = 30 mm. **Rys. 2.** Schemat (a) oraz poglądowy rysunek (b) zbudowanego urządzenia. Rozmiar komory wynosi: $\emptyset = 20$ 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 μ m and a specific surface area of ca. 15 m²/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.



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.

- 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;
- 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. 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 completly because of a significant



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 zgładu wykonanego w kierunku równoległym do kierunku wzrostu warstw. 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 perpendiculary 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. 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						
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
298.6 ± 119.3	290.8 ± 171.1	368.9 ± 154.4	-	335.6 ± 134.5	495.2 ± 215.8	714.6 ± 276.6
12 ± 4.2	42.7 ± 22.6	51.0 ± 21.5	-	9.4 ± 3.2	22.5 ± 5.3	34.6 ± 9.1
24.38	47.59	55.54	69.22	24.69	48.31	56.50
2.07	2.91	3.74	4.35	2.05	2.79	3.80
2.32	3.47	3.85	4.52	2.34	3.51	3.91
	10% vol. CY3Z, 4% B1000 298.6 ± 119.3 12 ± 4.2 24.38 2.07 2.32	Parameters of 10% vol. CY3Z, 4% B1000 20% vol. CY3Z, 4% B1000 298.6 ± 119.3 290.8 ± 171.1 12 ± 4.2 42.7 ± 22.6 24.38 47.59 2.07 2.91 2.32 3.47	Parameters of the obtain 10% vol. CY3Z, 4% B1000 20% vol. CY3Z, 4% B1000 30% vol. CY3Z, 4% B1000 298.6 ± 119.3 290.8 ± 171.1 368.9 ± 154.4 12 ± 4.2 42.7 ± 22.6 51.0 ± 21.5 24.38 47.59 55.54 2.07 2.91 3.74 2.32 3.47 3.85	Parameters of the obtained ceramination 10% vol. CY3Z, 4% B1000 20% vol. CY3Z, 4% B1000 30% vol. CY3Z, 4% B1000 40% vol. CY3Z, 4% B1000 298.6 ± 119.3 290.8 ± 171.1 368.9 ± 154.4 $$ 12 ± 4.2 42.7 ± 22.6 51.0 ± 21.5 $ 24.38$ 47.59 55.54 69.22 2.07 2.91 3.74 4.35 2.32 3.47 3.85 4.52	Parameters of the obtained ceramitrices 10% vol. CY3Z, 4% B1000 20% vol. CY3Z, 4% B1000 30% vol. CY3Z, 4% B1000 10% vol. CY3Z, 4% B1000 10% vol. CY3Z, 4% B1000 298.6 ± 119.3 290.8 ± 171.1 368.9 ± 154.4 $ 335.6 \pm 134.5$ 12 ± 4.2 42.7 ± 22.6 51.0 ± 21.5 $ 9.4 \pm 3.2$ 24.38 47.59 55.54 69.22 24.69 2.07 2.91 3.74 4.35 2.05 2.32 3.47 3.85 4.52 2.34	Parameters of the obtained ceramit matrices 10% vol. CY3Z, 4% B1000 20% vol. CY3Z, 4% B1000 30% vol. CY3Z, 4% B1000 10% vol. CY3Z, 1% PEG / 1% PVA / 1% POlapix 20% vol. CY3Z, 1% PEG / 1% PVA / 1% POlapix298.6 ± 119.3290.8 ± 171.1368.9 ± 154.4- 335.6 ± 134.5 495.2 ± 215.812 ± 4.242.7 ± 22.651.0 ± 21.5- 9.4 ± 3.2 22.5 ± 5.3 24.3847.5955.5469.2224.6948.312.072.913.744.352.052.792.323.473.854.522.343.51

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:

- 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, andthen 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 zgładu 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 zgładu 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.
- 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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