Journal of the European Ceramic Society xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Original Article

Breath figures decorated silica-based ceramic surfaces with tunable geometry from UV cross-linkable polysiloxane precursor

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ARTICLE INFO

Keywords:
Breath figures
Porous ceramic
Silicon dioxide
Silicon oxycarbide
Silicon oxynitride

ABSTRACT

Little has been published so far on the fabrication of porous ceramic films by using the Breath Figure method. In this work we explored the Breath Figure method to obtain ceramics with patterned surfaces. A UV cross-linkable polysiloxane was used to produce Breath Figures with tunable pore size. Pores formation, in terms of size and distribution on the polysiloxane films, were studied as a function of the concentration of the starting solution and time before UV irradiation. The polymeric breath figures were then pyrolyzed in controlled atmosphere to obtain, through the polymer-derived ceramic, PDCs, route the corresponding ceramic preserving the original porous surface. Pyrolysis under different gases, in particular air, nitrogen and ammonia, allows obtaining films of three different ceramic materials: silicon dioxide, SiO_2, silicon oxycarbide, SiOC and silicon oxynitride, SiON respectively.

1. Introduction

In recent years the Breath Figure (BF) process has been proposed as an easy way for the fabrication of materials with a porous patterned surface in the nanometer or micrometer scale [1]. The process has been mainly applied to polymers, sometimes enriched with some non-polymeric materials like nanoparticles, carbon nanotubes, small organic molecules and nucleic acids [2]. Films obtained by BF process are generally proposed as templates for inorganic materials [3,4], surface enhanced Raman spectroscopy (SERS) substrates [5], size based separation membranes [6], optical and optoelectronics devices [7], chemical power sources anodes for lithium ion battery [8], micropatterns of biological molecules [9], sensors [10] and, recently, also as substrates for cells adhesion and proliferation [11–14].

The possibility to generate patterned surfaces on ceramics in a fast and controllable way could be of high interest. The BF process itself is very simple and it's based on the casting of a solution composed of the chosen material dissolved in a low boiling point solvent onto a substrate placed in a humid environment. Immediately after the solution casting, the evaporation of the solvent determines the liquid surface cooling. The cooling leads to the condensation of the water vapor from the moist atmosphere onto the solution surface and to the formation of small water droplets that penetrate in the casting solution. Water droplets increase their diameter following a time relationship proportional to $t^{1/3}$, while the thermocapillary flow, produced by the Marangoni effect, induces the movements of the water drops to colder areas that reduce the surface energy [15]. The movement and growth of water droplets continue until allowed by the progressive increase of the viscosity of the solution. With the time the droplets density increases and they start to interact because of proximity, assembling, in optimal conditions, in a typical and highly ordered honeycomb structure. Even if always possible, droplets coalescence is prevented by the thermocapillary convection that induces the formation of a solvent vapor film between the drops. During this step, the entropy of the system decreases drastically due to the arrangement from a random to a close-packed honeycomb pattern. Finally, after the complete evaporation of the solvent and the water, a stable film with an ordered porous structure is obtained [16–18]. Each variable involved in this process is able to modify the final result. Combinations of parameters like the used solvent, the chosen substrate, the relative humidity and temperature, and the vapour flow rate are all crucial factors, both for achieving the BF formation and for determining the final film morphology in terms of

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http://dx.doi.org/10.1016/j.jeurceramsoc.2017.10.005
Received 13 September 2017; Accepted 1 October 2017

thickness, pores diameter, depth, number, shape, spacing and assembly order [2]. Unfortunately, all these variables can influence the overall kinetics of the process, which is usually interrupted when the viscosity of the polymeric solution becames higher than the superficial tension force that generate and conduct the process. One method to arrest the evolution of BF formation and to freeze the evolving pores and pattern is to use photocrosslinkable polymers as base materials that can crosslink after exposure to UV light [18]. The use of pre-ceramic polymers allows the conversion of the patterned film into a ceramic with a patterned porous surface, through a pyrolysis process in controlled atmosphere [19]. According to this route, a pre-ceramic polymer is first shaped into the desired form, crosslinked – either chemically, using a catalyst [20], or thermally [21] or with UV light [22] - and then is converted into the final ceramic through a pyrolysis process in inert ($Ar/He/N_2$) or reactive ($O_2/NH_3/CO_2/H_2$) atmosphere [23–26]. The shape of the component can be retained during the process therefore enabling the production of net-shape elements [27,28]. Different gas atmospheres influence the final chemical composition of the resulting polymer derived ceramics, PDC, and therefore ceramic with different properties, such chemical inertness, corrosion and thermal resistance or mechanical strength can be obtained [29,30]. One of the advantages of the PDC route is its high flexibility since allows producing different Si-based ceramics, such as silicon oxycarbide (SiOC), silicon oxynitride, (SiON) or silicon carbonitride (SiCN) by selecting the proper silicon-based polymer precursor and/or changing the pyrolysis atmosphere [19]. Accordingly, polysiloxanes pyrolyzed in O_2, N or NH_3 atmosphere transform into different ceramics, namely: SiO_2, SiOC and SiON respectively. The structure of these three materials is based on Si-centered tetrahedral: in the case of silica all Si corners are occupied by O atoms while in SiOC and SiON some O are replaced by C and N atoms respectively. Such modification of the silica structure results into strong modification of the mechanical, thermal and chemical properties [31–33]. Concerning the application of ceramic materials as bio-active coatings for biomedical prostheses, both silica [34] and silicon oxynitride have been proposed due to their proven osteoinductivity [35]. On the other hand, studies on silicon oxycarbides for bio-applications are still very few and there is only indication of their excellent hemocompatibility for these materials [36–38]. In this framework the realization of porous SiO_2-based ceramic films by using a fast and easy technique like Breath Figure coupled with the PDC route can be of high interest. Remarkably such an appealing process has been very little explored so far by the scientific community and only few papers are available in the literature [39–41]. The conversion of the pores patterned polymeric film into a porous ceramic can expand the applicability of the method to the fabrication of catalytic supports, optoelctronic devices, porous burners, energy storage and accumulation systems and hot gas filters or gas sensors [30,34,42,43]. In this work we used a medical grade UV cross-linkable silicone, Loctite® 5248™, for the fabrication of UV photocrosslinked BF films which were subsequently converted into Si-based ceramics through a pyrolysis process in three different atmospheres, namely air, N_2 and NH_3. Accordingly, silica, silicon oxycarbide and silicon oxynitride BF ceramic films were obtained and characterized.

2. Experimental

2.1. Materials and methods

To prepare porous silicone films by breath figures, as-received Loctite® 5248™ (AG & Co, Germany, Henkel) was dissolved in ethyl acetate (Sigma, USA, vapor pressure = 73 mmHg 20 °C) to obtain solutions with concentrations between 0,5 and 20% w/w (kept under stirring for 4 h at room temperature in the dark to prevent early crosslinking). The BF process was carried out in an aluminum chamber equipped with a PLEXIGLAS Solar® UV-light transparent on the top, as described by Maniglio *et al* [18]. To induce the silicone polymerization a UV LED Spotled 365/15 curing equipment was used (Photo/Electronics srl, Italy), with the emitting wavelength on 365 nm, matching the curing wavelength of the material.

Table 1
Variables tested for Breath Figure process with Humid Flow.

Variables	InvestigatedValues
Precursor Concentration	From 0,5% to 20% w/w
Solvent	Ethyl acetate, Chloroform, Dichloromethane, Dimethyl Sulfoxide, Hexane, Carbon disulfide
Surfactant	0.1 to 100% w/w of the silicone (HLB = 1 ÷ 6)
Substrate	Quartz, Glass, Poly ethylene terephthalate, Mica, Water, and Glass treated with oxygen plasma
Flow Rate	0,1 to 1,6 L/min
Pre-exposure Time	0 s to 20 mins
Vapour Temperature	25 °C to 70 °C
Humidity	60% to 99% RH

To introduce humidity inside the chamber a controlled flow of N_2 was forced into a gas bubbler to saturate the gas with water vapor. Flow rates between 0,1 and 1,6 L/min were used. To obtain BF a drop of the starting polymeric solution was cast on a quartz glass inside the chamber with a RH of ≈99%. After the drop cast, at specific times (pre-exposure time) UV-light was switched on to photo-crosslink the film. A complete list of the variables tested for the BF process is reported in Table 1. BF films obtained on quartz substrates underwent to a one hour pyrolysis treatment to induce the organic-ceramic transformation by using a silica tubular furnace (Thermo Scientific Heraeus) with an heating rate of 5 °C/min up to 900 °C in three different atmospheres (flow rate of 400 cc/min): air to obtain SiO_2 BF, inert N_2 gas to obtain SiOC ceramics and reactive NH_3 to introduce N and produce a SiON BF. The morphology of the resultant polymeric and ceramic BF, was characterized by optical microscopy and scanning electron microscopy (Zeiss Axiotech 100 and Zeiss Supra 40) after coating the samples with a thin Pt/Pd film. The formation of an ceramic amorphous material after pyrolysis was confirmed by collecting X-ray diffraction spectra using a Bruker D8 Advanced X-ray diffractometer with glancing angle Bragg-Brentano geometry using Cu kα radiation λ = 1,5418 Å at room temperature, range of 20–80° with a 0,02° step size and a dwell time of 1 s. Surface elemental analysis and bonding state of the ceramic BF films were investigated through X-ray photoelectron spectroscopy with a Scienta-Gammadate ESCA 200 equipped with a monochromatized Al kα X-ray source 1486,6 eV.

3. Results

3.1. Breath figure process

The investigated process variables combinations used for the fabrication of the BF silicon films have been reported in Table 1. Some of these greatly affected the pattern formation in terms of pores geometry and pattern regularity. Moreover, in some conditions BF figures didn't form. In the following representative results are reported and discussed.

3.1.1. Time before the exposition to the UV-light

The use of a UV-cross-linkable material allows to freeze any time the BF process simply by exposing the material to UV-light. This approach has been already proposed by Maniglio et al., [18] using different photo-crosslinkable acrylic materials and obtaining breath figure ordered patterned polymeric films. We investigated the BF formation by exposing the films to UV crosslinking at different times from casting. Results are reported in Fig. 1 where the SEM pictures of the films UV crosslinked after different pre-exposure times and for different starting solution polymer concentrations are reported. Results in Fig. 1a–i correlate pre-exposure time and pores diameter for a 5% wt. solution. After 9′ from casting (Fig. 1i), no further increase of the pores diameter was