Journal of the European Ceramic Society 36 (2016) 1091–1101

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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

Shaping by microstereolithography and sintering of macro–micro-porous silicon substituted hydroxyapatite

Marie Lasgorceix, Eric Champion*, Thierry Chartier

Université de Limoges, CNRS, ENSCI, SPCTS, UMR 7315, F-87000 Limoges, France

ARTICLE INFO

Article history:
Received 24 July 2015
Received in revised form
16 November 2015
Accepted 18 November 2015
Available online 28 November 2015

Keywords:
Porous bioceramics
Microstereolithography
Sintering
Silicon-substituted hydroxyapatite
Bone graft substitutes

ABSTRACT

Additive manufacturing of silicon substituted hydroxyapatite (SiHA) ceramics with controlled macro–micro-porous architecture by microstereolithography and sintering is reported. Due to the role of silicon in bone calcification, the incorporation of silicate in hydroxyapatite has become of interest for applications in bone tissue engineering. But, the shaping and the sintering of SiHA remain few studied. For the shaping process, the formulation of a photopolymerizable suspension and microstereolithography parameters were optimized. Adjustment of the sintering parameters allowed the production of ceramics with controlled open microporosity in a wide range of variation, while preserving phase pure SiHA. A dimensioning model that takes into account the overcure due to light scattering during photopolymerization and the shrinkages during sintering was established. Using this method, macropores of various cross-sections, within the size range of interest for bone ingrowth, were shaped demonstrating the efficiency of microstereolithography for the direct manufacturing of bioceramic scaffolds with accurate architecture.

1. Introduction

Synthetic hydroxyapatite (HA) ($Ca_{10}(PO_4)_6(OH)_2$) is commonly used as bone graft substitute because of its good biocompatibility and its faculty to conduct bone formation (i.e., cell adhesion, proliferation and differentiation) onto its surface [1,2].

According to the "diamond concept" described by Giannoudis et al. [3], in order to improve bone restoration, tissue engineering strategies involve porous scaffolds, growth factors, mesenchymal stem cells and an optimal mechanical environment. In this scheme, the architectural and microstructural properties of scaffolds are essential factors. An interconnected macroporosity, in the size range 300–600 μm, with interconnections of about 50–100 μm, is necessary for cell attachment, migration and proliferation within the implant, and for vascularization [4–6]. More, some studies showed increased osteoconduction, and even osteoinduction, in the presence of micropores in the macroporous architecture [7–12]. Cells are also sensitive to the geometry of the support on which they grow [13]. Very recently, Bidan et al. highlighted the effect of pore and surface curvatures on cell behavior [14,15]. But, the influence of macropore geometry and of open microporosity on cell behavior and vascularization remains misunderstood.

In this aim, model ceramic supports with multiscale porosity have to be manufactured with good accuracy. Vector-by-vector stereolithography (SLA), an additive manufacturing (AM) technology, was used by several researchers to produce 3D scaffolds with complex shapes for tissue engineering [16,17]. This technique consists of shaping parts layer-by-layer by scanning a cross-sectional pattern of the part on each layer using a UV laser beam. The principle is based on the photopolymerization of a photosensitive system. This method was mainly applied for the manufacturing of polymeric scaffolds. Indeed, as pointed out by Skoog et al. [17], "direct stereolithography of bioceramic composite scaffolds (or bioceramic-polymer) is difficult since the addition of inorganic components increases the resin viscosity; in addition, bioceramic particles may interfere with irradiation of the photo-polymer. Due to limitations on the bioceramic concentration via the direct stereolithography approach, a number of studies have utilized indirect stereolithography (e.g., fabrication of a negative mold using stereolithography)". Despite these limitations, this technique can be used for the direct fabrication of ceramic parts [18]. It has been successfully used to produce complex on demand cranial implants made of hydroxyapatite (HA) [19].

Projection microstereolithography (PμSLA) derives from SLA. In this case, the whole surface of each layer that must be polymerized

* Corresponding author at: Université de Limoges, CNRS, SPCTS, UMR CNRS 7315, Centre Européen de la Céramique, 12 rue Atlantis, 87068 Limoges Cedex, France. Fax: +33 555 87 50 23 04.
E-mail addresses: marie.lasgorceix@etu.unilim.fr (M. Lasgorceix), eric.champion@unilim.fr (E. Champion), thierry.chartier@unilim.fr (T. Chartier).

http://dx.doi.org/10.1016/j.jeurceramsoc.2015.11.020
0955-2219/

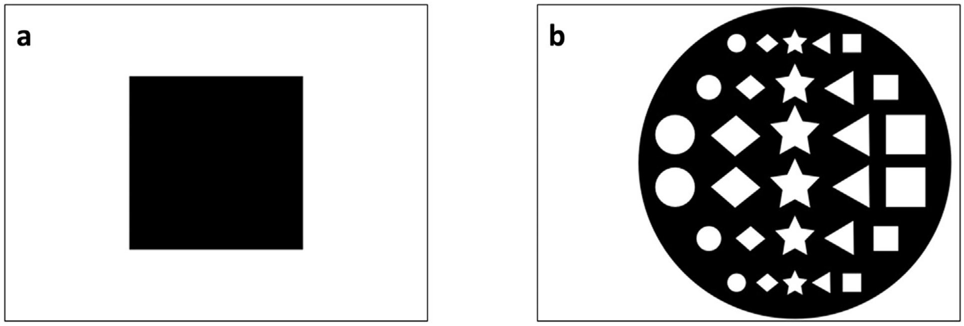

Fig. 1. Masks used for the shaping of model parts. The black portion corresponds to pixels "on", i.e., light oriented by the DMD toward the surface of slurry to be polymerized. (a) Configuration 1; (b) configuration 2.

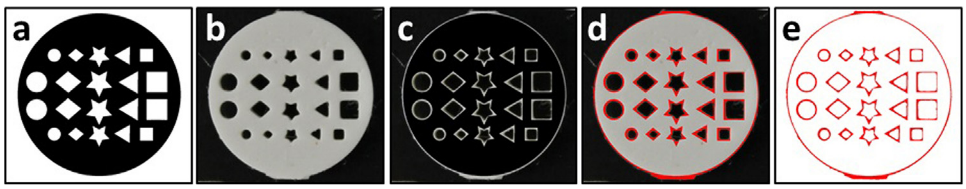

Fig. 2. Principle of overcure detection by image processing: (a) image of the mask, (b) photograph top view of a monolayer part shaped according to the mask, (c) superposition of the mask on the part photograph (d) red coloration of the overcured areas of the part (e) overcured areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

is fully illuminated by a UV light which is selectively reflected by a dynamic mask using an optical system [16,20]. Thus, PμSLA permits to reach a high geometric accuracy with a low building time [21]. Nevertheless, the same difficulties as those mentioned above arise. They come from the slurry formulation that must be optimized and from the interference between the UV light and the ceramic particles during the photopolymerization process of the resin. For ceramic particles loaded systems, the interaction between the UV beam and the photosensitive resin can be described by Jacobs equation (Eq. (1)). In this equation, the cure depth (C_d) relates to the incident energy (E_i), the critical energy requied for photopolymerization (E_c) and the penetration depth (D_p) as follows:

$$C_d = D_p \times \ln(\frac{E_i}{E_C}) \quad (1)$$

D_p illustrates the divergence from unloaded systems and takes into account the effects of interaction phenomena between the UV beam and the solid particles.

Chartier et al. [22] showed that the interaction of a UV light with ceramic particles loaded slurries was mainly governed by scattering phenomenon rather than absorption. This study investigated the influence of particle size and powder loading on the reflectance and transmittance values and established a relationship between the penetration depth (D_p) and the absorption and scattering coefficients. A quantitative model was proposed to predict the cure depth (C_d) knowing these coefficients. Other physics-based or experimental models for ceramic particles loaded slurries have been developed to describe light attenuation in the depth direction and to predict solidified layer thickness [23–25]. However, there is no physical model for light attenuation in the direction perpendicular to the incident beam, i.e., in the horizontal direction. Consequently, the lateral overcure phenomenon, in the horizontal direction and its consequences on the geometry of a ceramic part, cannot be anticipated. It is of prime importance to determine this effect in the case of complex geometries including angular zones. The monitoring and the quantification of roundness errors were proposed by Bail et al. [26] for the building of cylindrical features using unloaded resins. Kang et al. [27] proposed a model to predict solidified 2D horizontal pattern profiles for projection stereolithography technologies. This model appeared successful in the case of unloaded resins, but it cannot be applied to the curing of ceramic loaded slurries because it does not take into account the scattering effect due to ceramic particles. Only Gentry and Holloran investigated recently the cure width after curing straight lines of ceramic loaded suspensions [24,28]. But, to our knowledge, there is not any study reporting the monitoring and the quantification of the lateral overcure phenomenon during the shaping of complex and angular geometries such as those of interest for the pores structure in bioceramic scaffolds. Finally, little attention has been paid to the design of complex ceramic parts with accurate dimensions and geometries such as scaffolds. This requires a study of overcure phenomenon, optimization of the slurry formulation and precise adjustment of the shaping parameters.

Silicon substituted hydroxyapatite (SiHA) ($Ca_{10}(PO_4)_{6-x}(SiO_4)_x(OH)_{2-x}$) was chosen. Its biocompatibility was shown in a previous work [29]. Additionally, as stated by several authors, its bioactivity would be higher than that of pure HA [30–34]. Some of these results are discussed [35]. The doubts about the bioactivity of SiHA result from the incomplete material characterization (possible presence of secondary or amorphous phases containing silicon) and the lack of quantitative information concerning the *in vivo* Si release and its effect on bone growth. The incorporation of silicate groups in the apatite lattice causes formation of Si—OH groups at the surface of the material, which may constitute favorable sites to organo-alkoxysilanes used in the silanization step for the grafting of bioactive molecules [36,37]. This aspect constitutes an additional criterion for the incorporation of silicon in HA. Doubts and lack of knowledge about this material, promising for bone tissue engineering, lead researchers to better investigate it. But, up to now, the sintering of SiHA material has been the subject of very few studies [38–41] in contrast to the sintering of pure HA which is well known.

In this context, this work aimed at investigating the processability by PμSLA and further sintering of SiHA bioceramic parts with various geometries of macropores in the desired size range (300–600 μm) and with a controlled amount of open microporosity in a wide range of variation. It focusses on the analysis of overcure phenomenon during the photopolymerization, the sintering