

Research Article

Production of α -TCP Ceramic Precision Spheres for Mosaic-Like Ceramics Fabrication Use

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Abstract Profile accuracy of spherical α -TCP ceramics (artificial bone units) was improved by a precision fabrication method named “hydro-casting.” Hydro-casting shapes α -TCP slurry into spherical shape by dispensing definite quantity of α -TCP slurry in an oil and fixing the slurry’s shape by two-stage gellation. Resulting α -TCP spheres exhibit almost uniform shape and interunit gaps that would establish schematic features of porous body fabricated by “Mosaic-like ceramics fabrication (MLCF).”

Keywords α -TCP; porous; ceramics; spherical units; mosaic-like-ceramics fabrication

1 Introduction

Porous ceramic biomaterials, namely, “artificial bone” are achieving some mainstream acceptance in the field of regenerative medicine on hard tissues. Recently, the numbers of artificial bones and their manufacturing process are found on papers and webs, and the situation implies as if we affirmed acceptable artificial bones. However, there seem to exist unsolved issues in the situation of artificial bone-based therapy.

Unsolved issues are establishing custom-made method and assurance of high connectivity and geometrical features of pores in ceramic artificial bones. Because they are highly production-dependent matters, innovative production process that guarantees the issues is required. To address the innovation, we developed an original method for porous ceramics fabrication named “Mosaic-like ceramics fabrication (MLCF)” that fabricates porous ceramics in brick-like manner (Figure 1) [1].

MLCF fabricates intentionally designed (functionally designed if available) pores for each unit in a straightforward manner and integrates the units into custom-made shapes that patients require. Accordingly, air space in the resulting ceramics consists of intentional pores and interunit gaps that could be definitive geometries. More importantly, interunit

gaps could form a deductively proven one piece network (a perfectly connected pore network).

We have been demonstrated MLCF using calcium phosphate (CP) spherical ceramic units. In these cases, availability of custom shapes, precise unit packing, and even inter-bead gaps is dependent on sphericity and uniformity of units. That is to say, the spherical units should be produced with sufficient precision for ease-of-custom-made and regular interunit gaps. There are some ways to fabricate precision spheres, such as injection molding. However, most of these ways are costly that require specific apparatus. Moreover, we all know that aqueous slurry drops in oil form precision spherical shape. We, therefore, developed a precise fabrication method of spherical ceramic unit named “hydro-casting” to bring out CP slurry drops in oil keeping its spherical shape.

2 Materials and methods

“Hydro-casting” is an injection molding-like method that proceeds in the following 4 steps (Figure 2) (important features of hydro-casting are two different gellants in the slurry, and two stages gelling of the gellants):

- (1) preparation of CP slurry with two different gellants;

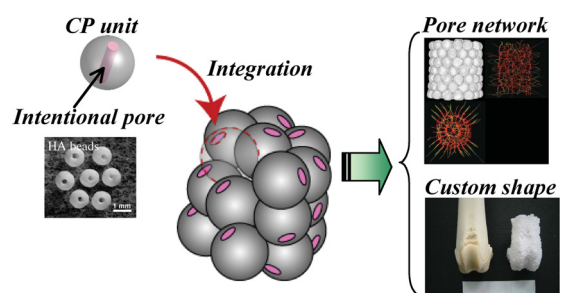


Figure 1: A schematic diagram of “Mosaic-like ceramics fabrication (MLCF)”.

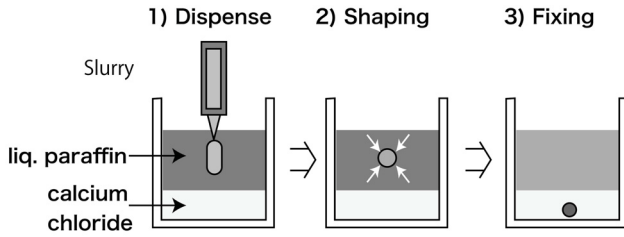


Figure 2: A schematic diagram of the hydro-casting.

- (2) quantitative dispense of the CP slurry into liquid paraffin on calcium chloride solution;
- (3) the dispensed CP slurry deforms into spherical shape by its surface tension;
- (4) dispensed CP slurry sinks into calcium chloride solution and fixes the spherical shape by gelling of the other gal-lants.

The slurry was prepared by mixing well-ground α -TCP powder (Taihei Chem. Ind. Co., Ltd, Japan), ultrapure water, and two different gellants (α -TCP concentration: 40 mass%). α -TCP was selected on the ground that α -TCP is one of well-accepted ceramic biomaterial and its grindability. The gellants are agar (Ina Food Industry Co., Ltd., Japan) and sodium alginate (Wako Pure Chemical Industries, Ltd., Japan). Agar is to prevent slurry's agglomeration and deformation at the boundary of liquid paraffin and calcium chloride solution. Without agar, slurry drops deform at the boundary forming a peak-like whipped cream. BA-50 agar, Ca free grade for bacterial cultivation, was selected not to fix sodium alginate in the slurry. Sodium alginate is to fix the slurry's spherical shape by a reaction with calcium chloride solution. Quantitative dispense of $4\ \mu\text{L}$ each was performed by a digital pipette. Resulting CP spheres were rinsed by ultrapure water and ethanol to remove liquid paraffin. CP spheres were dried at 333 K and sintered at 1673 K. Uniformity of the spheres was evaluated by standard deviation (Std) of spheres' long axis. The long axis of CP spheres and dried CP spheres were measured by image analysis based on optical image. Sintered CP spheres were observed by a scanning electron microscope (SEM). Crystal phase of dried CP spheres and sintered CP spheres were determined by an X-ray diffractometer.

3 Results and discussion

Figure 3(a) shows an optical microscope image of the resulting CP spheres before drying. CP spheres were seemingly uniform in outer shape without a peak, hence regularly formed intersphere gaps. Average length $\pm$ Std of long axes and aspect ratio (long axis/short axis) were 1.9567 ± 0.0278 , 1.0118 , respectively ($n = 20$). The Std

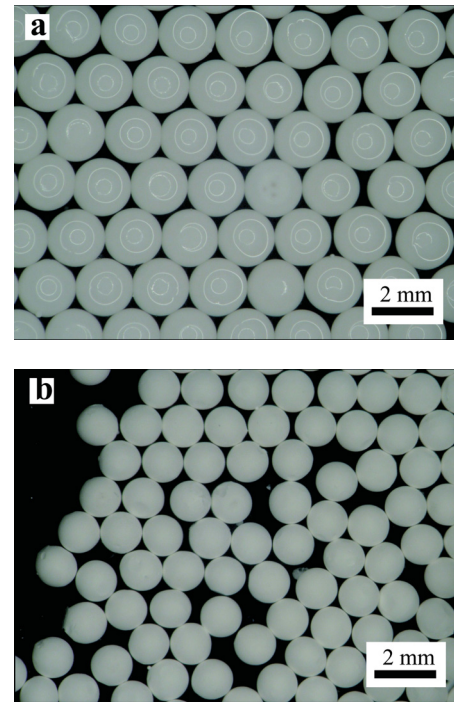


Figure 3: An optical microscope image of the resulting CP spheres before drying (a) and after drying (b). In both cases, CP spheres show sufficient uniformity and sphericity.

was only 1.4% of the average length, and the aspect ratio was close to 1, indicating high precision of the resulting CP spheres. When discussing about spheres' precision, the so-called "sphericity" is eloquent figure. In this case, the sphericity can be calculated by subtracting short axis' length from long axis' length, while the sphericity of the CP spheres was measured from 2D-based image analysis (to be precise, long and short axes should be measured from 3D-based measuring to calculate sphericity). The sphericity of the CP sphere was $23\ \mu\text{m}$, and the value was considered to fulfill a demand of MLFC with standard modeling resolution, while the value was not compatible with that of finest ceramic ball bearing.

The CP spheres shrank by 333 K drying, keeping its uniformity and sphericity (Figure 3(b)). Average diameter $\pm$ Std of the dried CP spheres was $1.325 \pm 0.0260\ \text{mm}$. Figure 4 shows an SEM image of the CP sphere after the sintering. Although CP spheres shaped under gravitational pressure, CP spheres were well densified, and no apparent grains' figure was remained in the surface of the CP spheres. This homothetic shrink and densification, favorable results, would provide MLFC with better accuracy and mechanical strength. The favorable results were not available in case of hydro-casting using stock α -TCP powder, meaning availability of fine α -TCP powder rules results of hydro-casting. CP spheres kept mostly α -TCP phase, but contain slight amount of hydroxyapatite phase. This is due to

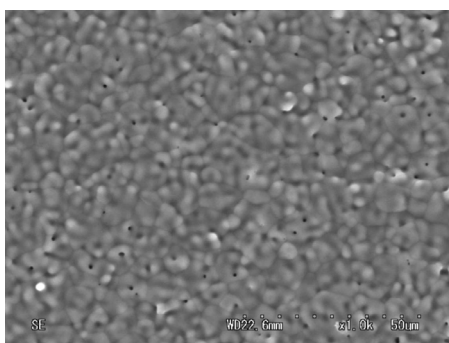


Figure 4: An SEM image of the CP sphere after the sintering.

hydrolysis of α -TCP in the calcium chloride solution. Minimizing HA contamination would be difficult because CP spheres require aging time in the calcium chloride solution to achieve a certain jelly strength to undergo 333 K drying.

4 Conclusions

We developed a precise fabrication method of spherical ceramic unit for MLCF named “hydro-casting.” Hydro-casting enables us to fix and take up spherical α -TCP slurry drops in oil by adding two types of gallants to slurry and two-stage gelling. The resulting α -TCP spheres showed sufficient uniformity and sphericity to form regular inter-unit gaps that are required for better MLCF. Consequently, the hydro-casting was considered as an essential production method of precision CP units for better MLCF.

References

- [1] K. Teraoka, Y. Yokogawa, and T. Kameyama, *HA beads for bone regeneration*, J Ceram Soc Japan, 112 (2004), pp. 863–864.