**Tailoring hydroxyapatite powder properties for 3D printing based on selective laser melting or sintering**

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***Highlights***

* The hydrodynamic parameters mainly impact agglomerates size distribution.
* Pure HAP can be produced ensuring relevant physicochemical conditions.
* An absorbing additive such as graphite may be used to increase HAP powder absorptance.

**1. Introduction**

The selective laser melting/sintering (SLS/M) as promising additive manufacturing (AM) technique allows the shaping of bioceramic parts as patient matched tissue engineering materials. These parts must have complex structures and ideal properties, like bioactivity and biocompatibility to ensure a good osseointegration/osseoincorporation of the implants, as well as good mechanical and chemical resistance. However, a deeper study of ceramic feedstock properties to achieve a better laser-material interaction during the shaping of the parts is essential to obtain an accurate control of the porosity, interconnected pores and to avoid the formation of cracks. For that, the production of nano-structured agglomerates is required in order to increase the surface and thus the reactivity required for effective sintering while keeping suitable flowability and dispersing properties. [1] Besides, ceramic powders absorptance at Nd-YAG laser wavelength (1.06µm) is not enough to produce a suitable heat/matter exchange between the particles to trigger the material densification. Improving the laser radiation absorption by means of use of absorbing additives is also of particular interest. [2, 3]

In this communication, we discuss the relationship between the hydroxyapatite (HAP) powder properties and the synthesis process parameters. Optimal purity, aggregate size distribution, and morphology of powder have been tailored in order to improve the laser-material interaction during 3D printing process of ceramic parts. Moreover, the influence of a commercial graphite (TIMREX KS44) as absorbing additive in the absorptance of HAP powder at Nd-YAG laser wavelength has been studied.

**2. Methods**

A scale-up of the HAP synthesis process was realized from a 1L reactor to a reactor of 4L. The precipitation of hydroxyapatite results from the reaction at a high temperature of phosphoric acid and calcium nitrate in an aqueous ammonia medium:

A double-jacketed cylindrical glass vessel, and three glass containers for the reactants (calcium nitrate, phosphoric acid and ammonia) compose the lab-scale apparatus. Initially a given volume of an aqueous solution of calcium nitrate is put into the reactor, then raised at the desired temperature for the synthesis. During a first period of the synthesis process, only ammonia is fed in order to increase the pH of the solution inside the reactor. Then during a second period, in which the synthesis itself is performed, the three solutions are continuously fed. At the end of the synthesis, the feeding of the reactants and of the ammonia solution is stopped but the system is maintained under stirring at high temperature during a maturation phase. Finally the reactor is drained, the particles are washed, during the suspension filtering itself done by suction through a Buchner funnel using a filter paper. The filtration cake is then freeze dried and calcined at 1000°C during 10 hours into an oven. This final step allows the drying of the crystallized HAP and the removal of any remaining impurity. For analysis purposes, samples are collected all along the process, as slurries to allow particle size distribution measurement, or as dried or calcined powders, to characterize the HAP purity.

Analysis of powder microstructural, chemical and physical properties was done by X-ray diffraction, FTIR, morphometer and SEM. The influence of the graphite (TIMREX KS44) as absorbing additive is studied by preparing different mixtures with the synthesized HAP and a mass of graphite in the range of 0% and 2.5% by mechanical mixing and measuring the absorptance at Nd-YAG laser wavelength.

**3. Results and discussion**

The effect of the stirring rate applied and the reactants flow rates was studied by analyzing the product recovered at the end of the synthesis process using different rates and different synthesis durations. The results showed that both parameters are closely related with the aggregate size distribution of the final product. A rather high stirring rate is needed to properly mix the reactants and get a product with a narrow size distribution around a few microns. The whole duration of the synthesis can be adjusted without affecting the product chemical purity ensuring a relevant pH regulation. A value of absorptance higher than 40% was observed from the mixture containing a proportion of 0.75% of graphite mass onwards showing promising results.

**4. Conclusions**

Stoichiometric HAP synthesis was studied varying physico-chemical and hydrodynamical conditions and analyzing their effect both on agglomerates size distribution and product chemical composition. The change in the absorption by graphite mixing was also analysed. A small proportion of graphite in the mixture is enough to obtain an absorption value close to the one observed in metal powders often used in SLS/M and it is expected to be higher enough for the use of the ceramic composite powder in AM technologies.

**References**

1. Monmaturapoj, N. Journal of Metals, Materials and Minerals 18 (2017).
2. Nikolay K., Yurii V., Rapid Prototyping Journal 6 (2000) 155-61.
3. Ferrage, L., Bertrand, G., Lenormand, P. et al. J Aust Ceram Soc (2017) 53: 11.