Title:
Rapid Prototyping and Thermal Gradient Method Applied to Fabrication Porous Structure for Application in Biomedical Field

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Introduction:
The objective of this work controlled porosity of Hydroxyapatite (Hap) ceramics for bio medical Application using thermal gradient and vertex tube for separation of solvent and two lasers are used Nd:YAG and CO_2.The energy absorbed for CO_2laser is about 20%,for Nd:YAG or famto second laser is Approximately 40-80% ,and using Q-switch technology power of laser and over all process can control effectively. Along with main nozzle transient controlling function two nozzle are added one for solvent and one for powder.

Porous Hydroxyapatite (Hap) is expected to have desired mechanical and biological properties for biomedical applications. However, due to material processing problems, to date, this material can only be prepared by conventional techniques which are time consuming and unpredictable specially controlling porosity and density which highly recommended factor for biomedical application.

Three stage heating with two laser arrangements for gradual temperature change so that transformation is is faster but diffusion is limited to surface diffusion only.

Primary result shows mechanical properties and porosity is as per bone structure. The micro structural characterizations such as phase purity and composition of porous BCP granules were performed and verified by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) analysis. The chemical and microstructural information of fabricated structure were investigated by by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) Scanning Electron Microscope (SEM).

Using this technique, it is possible to produce scaffolds with mechanical and structural properties close to those of the natural bone and teeth. The prepared scaffold has an open, regular pattern and uniformly interconnected porous structure. Some extent problem of small Nano particle aggregate together is called Balling and product of different temperature solidify on the layer is called recasting is dominates the process. By optimizing the operating parameter these problem can be minimized.

The main challenge for rapid fabrication of Biomaterial by Rapid Prototyping (RP) is the preparation of exact pH, viscosity, density slurry. Since settle time for Hap is small hence apparent density changes continuously.

In this beam is stationary and platform is moving and heated uniform continuously. In Primary heating a laser beam is used to directly bind the powder without addition of binder .The powder is heated to temperature ($Tm/2$) at which fusion of particle takes place .The process continue with formation of neck between the adjacent particles. In This RP Process primary laser Nd:YAG laser is for melting (Fusion) and for consolidation $CO_2$is used. To have non skinning binder system mixture is heated in Nozzle so that by thermal action resin (binder) will separate out.

3-D computer graphics (Catia V6) is used to prepare model and exported as stereo lithography (Stl) format. Rectangular scaffold were made of size 15mmX6mm.

The LSD process utilizes a .stl CAD file to define the geometry of an object to be fabricated. According to thickness cross section is sliced into number of thin layer. Each scanned layer represents a cross section of the sliced CAD model with stereo lithography (Stl) format. Finally, an object is integrated by sequentially thermal bonding the layers with a scanning laser beam.

Rapid prototyping (RP) and thermal gradient is used to fabricate Porous hydroxyapatite (Hap) by depositing on substrate material like alumina, Titanium. Main efforts were directed towards development of Pure Hap crystalline, chemically compatible and stable bioactive film on bioactive substrate structure at elevated temperature.

The slurry is then made pass through specially designed nozzle and heated to predetermine temperature. While deposition primary laser Nd:YAG laser is used for heating which heats the slurry up to $T_m/2$ temperature. Then secondary laser CO_2 laser heats up to 1300^0C. While rapid heating is done by primary laser Nd:YAG laser and secondary laser CO_2 laser along with heating enhances gas blowing, PH increment, which is accelerated by crosslinking agents decomposition, provides better cross linking. Thus, interconnected and well defined macro porous structures were produced easily and rapidly.

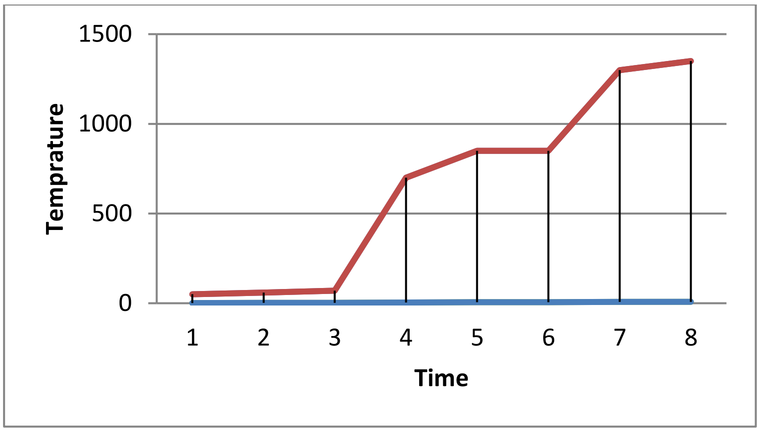

Fig. 1: Three Stage heating of Slurry.

Experimental Construction and Working:

To promote porosity favorable conditions are i) lower temperature (500^0C) pore growth occurs, but without densification. ii) Large pore size, it is difficult to remove. As a general guide line, a pore size more than half the grain size is promotes porosity in most materials (J Zheng1989) (T S Yeh 1990).

The critical conditions for pore shrinkage or growth are decided by the dihedral angle and coordination number (JE Blendell,CA Handwerker 1986). For maintain porosity the dihedral angle must be high, further grain boundary extension causes increases the system energy.

The process of mimicking the native structure of porous structure has been simplified greatly by recent advances in three dimensional (3D) imaging.

The STL file is then converted into the file format for the relevant RP machine using Magic (Materialise) and the 3D model was then constructed

This research takes a fluid dynamics approach to fabricate porous structure by using the RP. This will be achieved through analyzing the main nozzle (Figure 2). The print material is biocompatible material, is prepared using resin, disperent, and cross-linking agent. As shown in fig.1.the tapered cylindrical sectionneedle is used as the extruder is called the liquefier, which is connected to heating elements that melt the Slurry prior to extrusion. The brass liquefier is actually the central area of focus since its internal geometry serves as the flow channel for the melt.

Primary laser Nd:YAG will heat the slurry up to $\frac{T_m}{2}$ although power density is control by computer controller.

Computer controller takes feedback from raw slurry and considers various physical properties like green density, apparent density, and viscosity of slurry. As per programming of porosity, mechanical strength and other characteristics computer controller adjust slurry and air flow to maintain % wt. of powder.

Eight channel data acquisition system is used for data acquisition provides feedback of temperature, pressure inside chamber. According to feedback computer controller maintain scanning speed and laser power density.

For Second CO_2laserbeams of higher energy densities and shorter pulse duration causes shockwaves resulting from resulting recoil pressure. This creates the hydrodynamic melt motion on the liquid melt pool underneath; there exists strong temperature gradients in the molten material. Due to Gaussian nature of laser beam which creates high temperature at Centre than at edges as result the melted layer ejected out from center of the melt pool and creates a crater as shown in figure. As laser is switched OFF melted layer at edges tends to come back to its original place due to gravitational and surface tension forces. Simultaneously, the molten layer tends to solidify rapidly due to the thermal gradient effects.

There is a relation is a between grain size G, pore diameter d_p, and fractional porosity V_p

$$\frac{G}{d_p}=\frac{K}{RV_p}$$

Where, R expresses the ratio of attached pores to randomly placed pores, and K is a geometric Constant. Values of R range from 1.7 to 5.7 for various materials. Note that the degree of boundary-pore contact remains essentially constant during sintering.

As liquid-phases heating by Secondary laser progresses, the large grains grow by dissolution. Dissolution makes the smaller grains spherical. Low-energy crystallographic orientations are favored, leading to faceting of the grains, Further, in systems where the surface energy varies with crystallographic orientation by more than approximately

15% , angular grain shapes are expected(A Radon 1979). The shape observed in random cross section depends on the orientation with respect to the section plane.

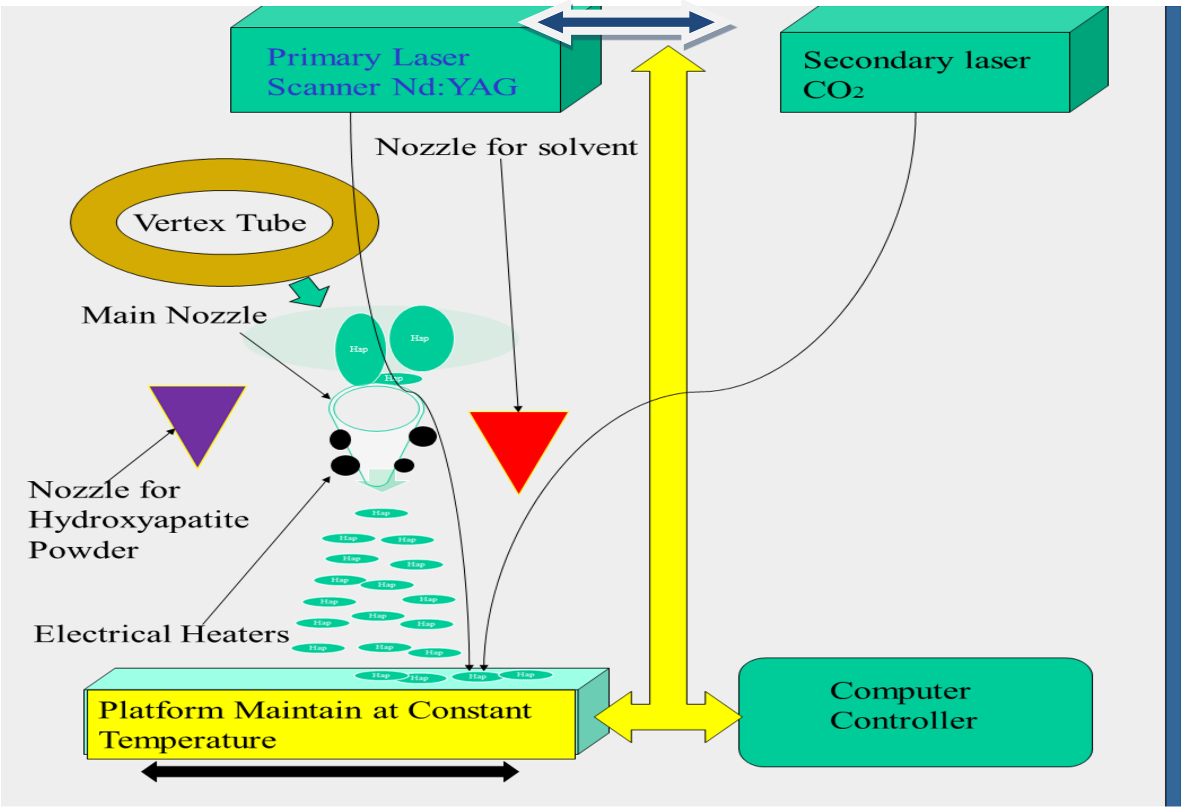

Fig. 2: Experimental arrangement.

HA & TCP Nano particles considered widely in the development of biomaterial due to Osseo integration, Osseo conductivity, Nano size effect and biomimetic resemblance to natural bone structure.

<u>Nozzle Design Consideration for biomaterial Fabrication:</u>

The physical; properties of slurry are probably the most vital aspect of biomaterial fabrication.

Viscosity, surface tension, &inertia plays vital role in fabrication which effects behavior of droplets & liquid jets.

Balance is to be maintained between low viscosity to have uniform flow & surface tension should be high to avoid ink dripping from the nozzle.

As shown in Fig.3 (a) slurry prepared with solvent resin and dispercening agents and cross linking agent will pass through specially designed Vortex tube consist of perforated pipe wounded in circular manner because of centrifugal force excess liquid will separate out and only pure ,homogeneous slurry will pass on to Main nozzle.

As shown in fig.3 (b) as per demand of transient condition, drop on demand nozzle 1 will operate. If temperature of molten pool is higher than require it will causes completely burn out of Slurry.

At this stage drop on demand nozzle 1 will eject raw and coarse HaP powder which will provide rapid cooling and also promotes surface diffusion.

Some dimension less number a) Reynolds b) Weber c) Ohnesorge(oh) are used for describing and analyzing jetting & break up phenomenon in droplet generation.

$$Oh=\sqrt{\frac{We}{Re}}$$

$$=\frac{n}{\sqrt{\rho\sigma d}}$$

"Oh" describe relative importance of viscous & surface force

n – Dynamic viscosity,

ρ - Density

σ -Surface tension

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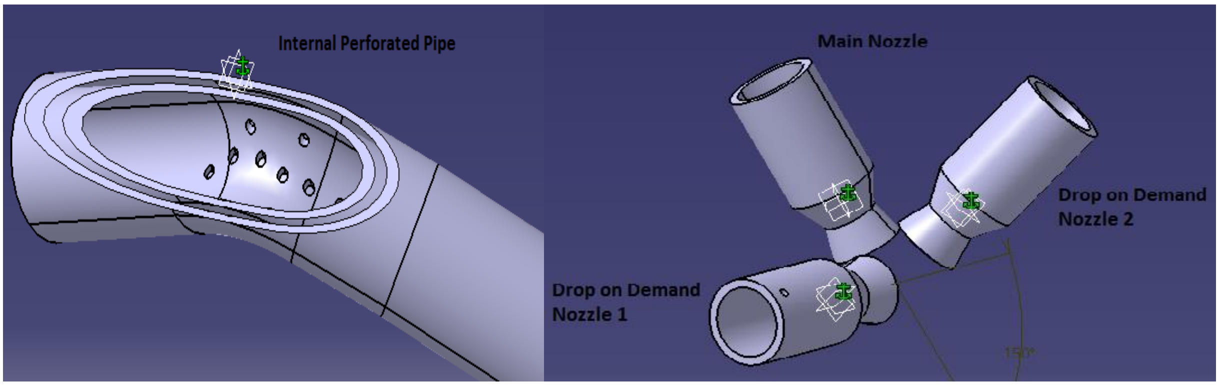

Fig. 3: (a) Perforated pipe, (b)Three Nozzle arrangement.

Oh> 1 fluid viscosity dissipation result in nozzle clogging & impedes ejection of drops.
Oh< 0.1 multiple drops instead of single well define drop.
Criteria for precision of fabrication
1 >Oh >0.1corresponding droplet velocity should be 5-10m/s.
The Nano particle should have size 100 times of nozzle to avoid clogging
Droplet formation is related to viscosity of Nano particles.sphrical shape is influenced by surface tension.
Viscosity 2-30 Mpa-s. Surface tension upto 60mN/m is acceptable

Heating and melting Stage
Initial melting is takes place at the surface if heating is too rapid. Thermal stresses may cause part cracking. This can be avoided using heating with electrical heaters around syringe. Primary Heating with Nd:YAG laser layer melt, it flows in the inter-particle pores and subsequently can penetrate the grain boundaries in the particles.

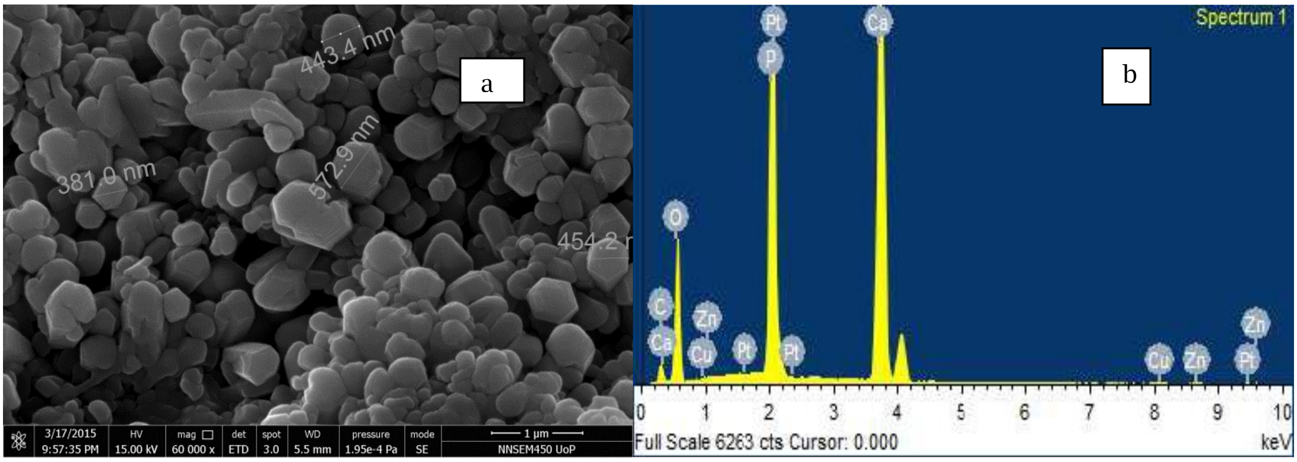

Fig. 3: (a) SEM image (b) EDX results of Hap.

Conclusions:
The rapid prototyping (RP) and thermal gradient can be commercialized for fabrication of scaffolds which have superior properties for bone tissue engineering. The SEM & EDS indicate uniform and regular distribution of Hap, calcium carbonate, phosphate product. It's showing bonding with zirconium, titanium best interfacial bonding is getting with Copper. Therefore, the current modification method may provide a better feasible solution to fabricate HAP as one substitute material with high interfacial bonding and performance. Many small Nano particles aggregate together to form one higher sized micro particle is called Balling and product of different temperature solidify on the layer is called recasting is dominates the process. By optimizing the operating parameter these problem can be minimized.

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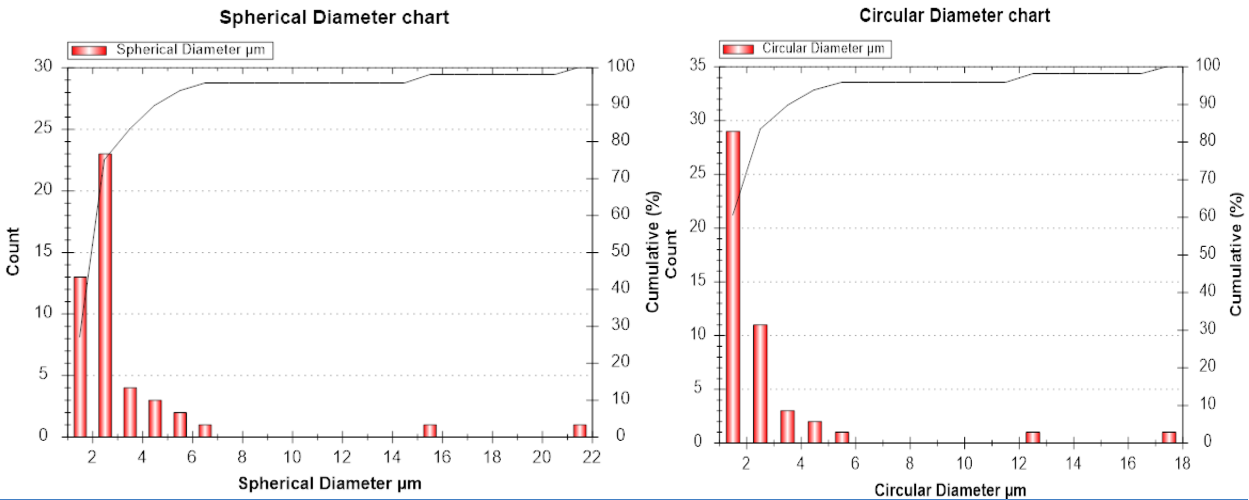

Phase 1 Grain Size ASTM E-112-96 Planimetric Method

1	Number of grains per mm	Na	31358.885	1/mm²
2	Average grain area	AM	31.889	µm²
3	Average diameter of grains	DM	5.647	µm
4	Number of intercepts per mm	NL	198.777	1/mm
5	Mean linear intercept line	LM	5.031	µm
6	ASTM Grain Size Number	G	11.983	G

Fig. 4: SEM Analysis of grain structure.