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Effect of Sintering Temperature on the Properties of Porous Alumina Synthesized through Soft Combustion for Biomedical Application

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Abstract— This paper describes the effects of sintering temperature on porous structure of alumina produced by using different types of fuels (urea and glycine) through a soft combustion reaction. In the present work, the effect of sintering temperature on alumina properties is studied. The porous alumina which is sintered at various temperatures (1250°C, 1350°C, 1400°C and 1500°C) is compared to determine the optimum properties that can be applied on implant applications. Phase identification through X-Ray Diffraction (XRD) shows an alpha alumina phase is obtained in all samples. X-Ray Fluorescence (XRF) result supports the obtaining phase. Mechanical property is determined using Modulus of Rapture (MOR) which shows that synthesized porous alumina sintered at 1500°C shows higher flexural strength (18.37 MPa) compare to other temperature. However, as the application aims for the biomedical implant, the porous structure of synthesized alumina is another factor to be considered as if it structured well for the application. Through the morphology observation using Field Emission Scanning Electron Microscope (FESEM) on sintered bodies, overall, the result shows that the porous structure of alumina sintered at lower than 1500°C shows better structure in terms of to be applied in implant.

Keywords: Porous Alumina, Soft combustion, Implant application, Sintering temperature, X-ray Diffraction (XRD)

I. INTRODUCTION

Alumina is one of the ceramics that is compatible with the bioceramic implants. It is also known as one of the bioinert materials, which has been studied for many medical applications such as cell carriers, artificial organs and hip joints [1-3]. The successful of these implant depends on requiring and retaining stable fixation of the device in the bony site [1]. In order to ensure that, porous structure is an important structure tool as it will provide biological fixation. The structure allows tissue ingrowths into the pores throughout the implant. It also increases the interfacial area between implant and tissue, and increase resistance of device's movement in implantation. Therefore an established interface can be obtained by living tissue in pores [4]. Alumina produced by soft combustion method has high percentage of porosity. The combustion method is an easier process to reveal porosity as it evolves gaseous during the process. Combustion synthesis has been studies by several scientists through years. Advantages of the combustion process are it produces high purity powders by simple technique at a short time and energy saving. Besides, the gaseous released during the process are only N_2, CO_2 and H_2O gases which make the combustion is an environmentally clean process [5-7]. As this combustion process involves only smoldering at the bottom of the container, it is termed as soft combustion process. In synthesizing porous material by combustion process, besides the effect of different fuel types, sintering temperature is also one of the factors that can affect the properties of the porous structure. Sintering mechanism can change the structure as it involves sintered bonding between the particles that cause shrinkage, changes in pore size, pore distribution and affected the mechanical properties of porous alumina. In this paper, different temperatures are used to study the effect of sintering temperature on the synthesized porous alumina.

II. METHODOLOGY

Aluminium nitrate ($Al(NO_3)_3.9H_2O$) and two types of fuels, glycine ($C_2H_5NO_2$) and urea (CH_4N_2O) were mixed in the required stoichiometry ratios in a minimum volume of deionized water to obtain transparent aqueous solutions. The sample was thermally dehydrated at 80°C on a hot plate to remove the excess solvent and resulted in the viscous liquids. As soon as the viscous liquids were formed, the temperature of the hot plate was increased to ~200°C. At this stage, the viscous liquids swelled and auto ignited, with the rapid evolution of a large volume of gases to produce

fluffy powders hereafter terms as as-synthesized powder. The nature of ignition was dependent on the fuel-to-oxidant stoichiometry ratio for each fuel and the ratios were according to the concept of propellant chemistry. In order to remove traces of undecomposed products, the as-synthesized powders were calcined at 1100°C with 2 h soaking time in air and 5˚C/min ramp speed to obtain pure and stable phase alumina powders. The alumina powders that obtained were named as AG (glycine as fuel), and AU (urea as fuel). X-ray diffraction was performed on the calcined powders for phase identification by using Cu-Kα radiation of wavelength 0.154 nm. The scan angles ranges from 10° to 90° with a scan speed of 1°/min. Silicon was used as an external standard for correction due to instrumental broadening. In performing MOR to determine the flexural strength of the samples, the powders were pressed into 55 x 10 mm at 150MPa and sintered to different temperatures in the high temperature carbolite furnace RHF1400 in air. The MOR testing was dperformed at 0.5 mm/min crosshead speed and 40mm of the spams distance. The microstructures of the fracture surface were investigated by ZUPRA VPFSEM scanning electron microscope.

III. RESULT

Alpha phase spectrum was obtained from calcined powder, as shown in Figure 1. From the spectra a single-stable phase of α-alumina was obtained for both samples. Crystallite size which measured by X-ray diffraction following Scherrer's formula:

$$D = 0.9\lambda/\beta\cos\theta \qquad (1)$$

where D is the crystallite size in nm, λ is the radiation wavelength (0.154 nm), θ is the diffraction peak angle, and β is the line width at half peak intensity. β can be calculated using the following formula:

$$\beta = \beta^2_m - \beta^2_s \qquad (2)$$

where β_m is the measured full width at half maximum (FWHM) and β_s is the FWHM of a standard silicon sample ($[3.06 \times 10^{-6}]^{1/2}$).

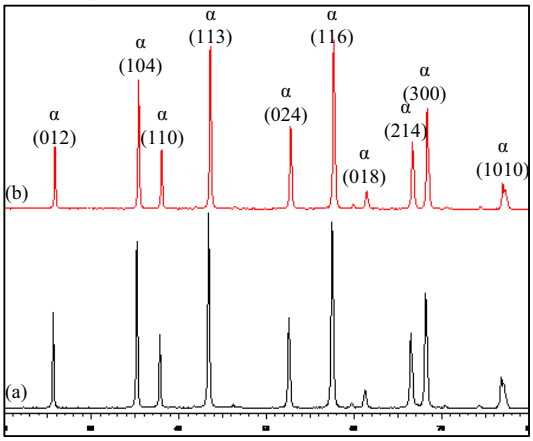

Figure 1. Shows the XRD spectrum of single-phase α-alumina powder by different type of fuels: (a) urea (AU), and (b) glycine (AG).

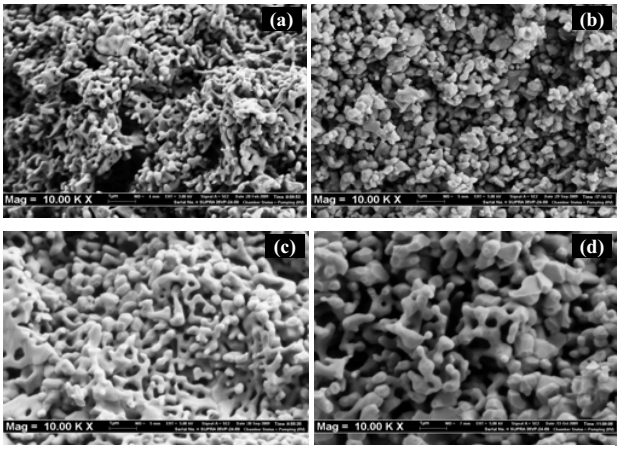

Figure 2: Microstructure on a fracture surface of porous alumina produced by glycine as a fuel (AG) was sintered at (a) 1250°C, (b) 1350°C, (c) 1400°C and (d) 1500°C.

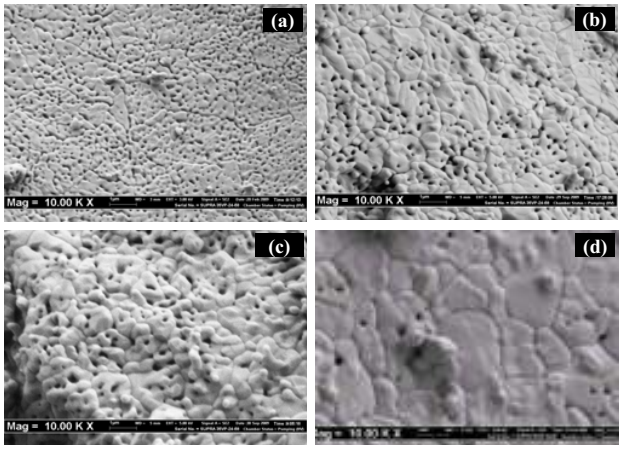

Figure 3: Microstructure on a fracture surface of porous alumina produced by urea as a fuel (AU) was sintered at (a) 1250°C, (b) 1350°C, (c) 1400°C and (d) 1500°C.

Table 1 shows that AU has smaller crystallite size compared to AG.

Table 1. Intensity and crystallite size of as-synthesized powders calcined at 1100°C.

Samples	Crystallite size
AU	80.92 nm
AG	99.82 nm

The morphology studies of porous alumina produced by glycine and urea as fuels respectively, sintered at difference temperature were shown if figure 2 and 3. It shows that the porosity becomes lesser with increasing temperature. However, in contrast, the pore sizes increase with increasing sintering temperature (Figure 4). Except for AU the pore size decreases from 290.3 to 268 nm after sintering at 1500°C. AG shows the highest relative pore size that is 558.3 nm when sintered at 1500°C.

Figure 4 shows the linear shrinkage of samples sintered with varying temperatures. With increasing temperatures, the compact samples shrunk increasingly. The shrinkage of samples changed from 0.5 to 7.1% for AU and significant changes for AG which is from 1.3 to 13.5% when the sintering temperature increased from 1250 to 1500°C. For

AG the shrinkage between temperatures of 1400 to 1500°C is slightly larger compare to others.

Figure 5 shows the flexural strength of sample sintered at different temperatures (1250, 1350, 1400 and 1500°C). The flexural strengths were enhanced with increasing of sintering temperature for both samples Au and AG. At temperature relatively between 1400 and 1500°C, the flexural strength of AU is much higher than AG.

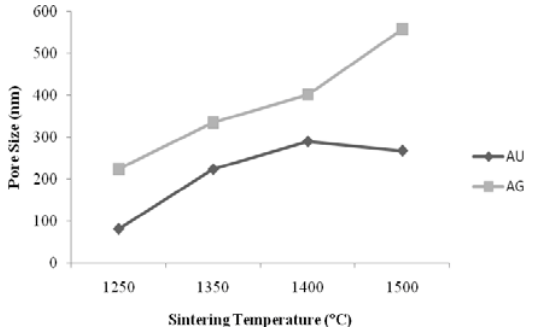

Figure 4. Pore size of samples sintered at 1250, 1350, 1400 and 1500°C

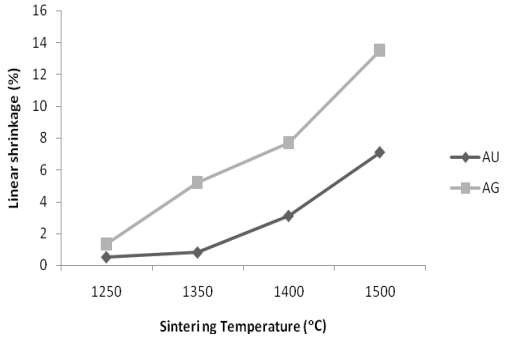

Figure 5. Shrinkage of samples sintered at 1250, 1350, 1400 and 1500°C.

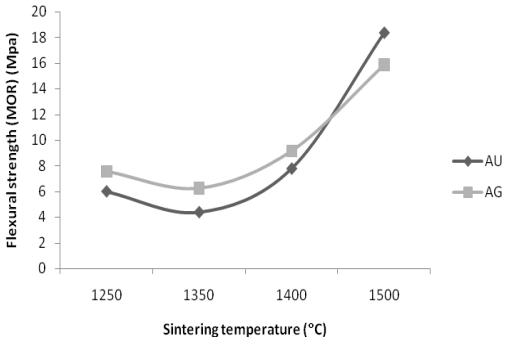

Figure 6. MOR of samples sintered at 1250, 1350, 1400 and 1500°C

IV. Discussion

Figure 1 shows the XRD spectra of porous alumina synthesized by using two types of organic fuels. The spectra show that porous alumina produced by using glycine and urea as fuels, the product have single-phased alumina. Thus, different types of fuels do not affect the purity of alumina produced. The crystallize size of AU and AG powders were calculated using Scherrer's formula shows that AU has lower crystallite size compare to AG.

The dimensional change in a powder compact is one of the most widely applied sintering monitors. Although in many situations sintering is intentionally performed to bond particles without significant dimensional change, there are great many situations that cause shrinkage. The shrinkage is caused by the particles which initially packed loosely, approached and contacted during sintering [8]. As the particles contacted, it performed neck growth which somehow change the particle size. In the formation of necking, the grain boundary and particle surface diffused. As sintering temperature increase, the grain boundary diffusion and surface diffusion are enhanced. Hence, it increases the particle size. Meanwhile, the bulk transport process decreases the interparticle spacing as neck growth processes, resulting in compact shrinkage and the formation of additional new necks.

As seen in the figure 3, the grain growth become more significant with increasing sintering temperature as the grain boundary diffusion is enhanced. The grain growth were then decreased the porosity as pores on the grain boundaries were drag by the motion until pore-boundary separation formed, which left the spherical pores inside the grains (see figure 3(d). At low initial packing densities, particles bond to form long-chain open pore structure that exhibit grain growth but fail to undergo densification (as seen in figure 2). This event was called as coarsening process [9].

In coarsening process, the pore size increased even when the porosity decreased. Increasing the sintering temperature, the pore growth occurred with rapid densification and caused the local densification (densification of small area) formed the agglomerated structure. This local densification open large flow channels between agglomerates. The agglomeration resulted in loosely packed and therefore increased the pore sizes [10]. Pore size of AU decreased obviously between 1400°C and 1500°C as there was no obstacle of agglomeration for pores to shrink.

The porosity, pore size and grains contacting area are keys affecting the strength of porous alumina. The calculation of the flexural strength (MOR) was based on the calculation by using the equation below:

$$\sigma = \frac{3PL}{2bd^2} \qquad (3)$$

where P is Load of fracture (N), L is Distance between the support points, b is specimen width, d is specimen thickness.

AU sintered at 1500°C has smaller pore size compared to AG. Through the SEM images, the pore size of AU sintered at 1500°C have more contacting area as grain grew up. Hence, the alumina strength was enhanced.

V. Conclusion

From this study, the porous structure from the sample using glycine as fuel shows high surface area with open pore structure and evenly pore distributed with increasing temperature. This is potential structure for the implant application. While AU, even though the samples sintered at

1500°C has higher strength, however the performance of its porous structure in terms of to be applied in implant might be quite low as there is no significant open-pore distribution.

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