Effects of Milling Speed and Sintering on the Formation of Akermanite (Ca$_2$MgSi$_2$O$_7$) Bioceramics

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Abstract. The aim of the present work is to study the effect of different milling speeds on the preparation of akermanite ceramics. In this study, akermanite (Ca$_2$MgSi$_2$O$_7$) was synthesized by high speed planetary ball milling and mixing method. Calcium oxide (CaO), magnesium oxide (MgO) and silicon dioxide (SiO$_2$) were used as initial reactants. The starting materials were milled with molar ratio of 2:1:2, respectively, using ball-to-powder ratio 10:1 at different milling speeds of 300 rpm, 400 rpm and 500 rpm. After synthesis, the powders were pelletized to form pellets (13 mm) with 150 MPa by uniaxial pressing. The pellets were then sintered at 1250°C for 3h. Phase analysis by X-ray diffraction (XRD), surface morphology by Field Emission Scanning Electron Microscopy (FESEM), Brunauer-Emmet-Teller (BET) specific surface area analysis, linear shrinkage, porosity and density measurement were performed on the milled and sintered samples. It was found that milling at 500 rpm resulted in powder with largest surface area (108 m$^2$/g), indicating the finest size of powder. FESEM observations showed that the sintered-akermanite ceramics from 500 rpm milling at 1250°C were the densest with microcrystalline appearance and clear grain boundaries, while milling at 300 rpm and 400 rpm showed some pores in the sintered samples.

1. Introduction

Bioactive materials, especially calcium phosphate (CaP) and calcium silicate (CS) materials, have been investigated due to their excellent biocompatibility and osteoconductivity [1,2]. Among CS biomaterials, akermanite (Ca$_2$MgSi$_2$O$_7$), a mineral containing Ca, Mg and Si, has recently received research interest due to its better mechanical properties compared to hydroxyapatite (HA) [3] and it has common degradation rate compared with other silicate bioceramics [4].

Wu. et al. produced akermanite bioceramics in sol-gel method at sintering temperature at 1370°C for 6h. Their results demonstrated that akermanite samples have apatite-forming ability on their surface when soaked in simulated body fluid (SBF) for 10 days, and possess improved mechanical properties compared to HA [5].
Many methods have been proposed for the synthesis of nano-sized calcium silicate materials such as sol gel, chemical precipitation, hydrothermal and solid reaction methods [6-9]. Among them, mechanical activation is a technique used for a wide range of preparation of nano powders and composites with reduced particle sizes [10-13]. The objectives of high energy mechanical ball milling and mixing are for reducing the particle size and simultaneously mixing the raw materials. Besides low cost process, the advantages of this technique are simplicity of experiment, and rapid and easy to synthesize the products [14]. Most of the researchers have focused on the influence of milling time on particle size and densitification parameters [15,16]. The current study is therefore designed to study the effect of different milling speeds via high energy wet ball milling and mixing as a processing technique and subsequent sintering process on the formation of akermanite.

2. Materials and Methods

2.1 Samples preparation

In this study, akermanite powders were synthesized by using calcium oxide (CaO), magnesium oxide (MgO) and silicon dioxide (SiO2) as the starting materials with molar ratio of 2:1:2, respectively. These materials were then ball-milled with milling speeds of 300, 400 and 500 rpm for 4h (based on earlier study) in a planetary ball mill (Retsch PM 100). Zirconia balls were used as the milling media to assist the milling-mixing process. The ball-to-powder weight ratio was 10:1 and the deionized water-to-powder weight ratio was set to 4:1. Then, the resultant slurry was dried in an electric oven at 100°C for 24h, and subsequently ground and sieved. Some as-milled powders were used for BET specific surface area analysis and some were uniaxially pressed at 150 MPa to obtain disc-shaped green bodies with diameter 13 mm. The pellets were then sintered in an electric furnace at 1250°C with a heating rate of 5°C/min for soaking time 3h.

2.2 X-ray diffraction (XRD) analysis

The phase identification, lattice parameter and crystallite size of as-milled and sintered powders were obtained with Cu-Kα1 radiation on X-ray diffraction analysis (XRD, Bruker D2 Phaser, Germany). The obtained experimental patterns were compared with the standards compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS). The average crystallite size of as-milled samples was obtained from the experimental XRD patterns using the Debye-Scherrer’s relation [17],

\[ D = \frac{k \lambda}{\beta \cos \theta} \]

where D is the crystallite size for the (hkl) plane, \( \lambda \) is the wavelength of the incident X-ray radiation (Cu-Kα1 radiation, \( \lambda = 0.154 \) nm), \( \beta \) is the full width at half maximum (FWHM) in radians, and \( \theta \) is the corresponding angle of Bragg diffraction.

2.3 Field Emission Scanning Electron Microscopy (FESEM) analysis

Morphology and grain sizes of samples were investigated by using FESEM (Zeiss Supra Gemini 35 VP). A thin layer of gold (Au) samples was coated onto the sample. The average grain size of the sintered samples was evaluated using the image analysis software (Image J 1.51k).

2.4 Linear shrinkage measurement

Diameter \( (D_s) \) and thickness \( (T_s) \) of the green bodies were measured by digital vernier caliper (Mitutoyo, Japan). After sintering the pellets at 1250°C, the measurements of diameter \( (D_g) \) and thickness \( (T_g) \) of the samples were done again to evaluate the linear shrinkage of sintered samples. Changes in linear shrinkage of all samples during sintering was calculated by using the following equations [18]:

\[ \text{Diameter shrinkage (\%)} = \frac{D_g - D_s}{D_g} \times 100 \% \]

\[ \text{Thickness shrinkage (\%)} = \frac{T_g - T_s}{T_g} \times 100 \% \]
2.5 Porosity and density measurements

The apparent porosity $P$ measurement of the sintered akermanite samples was carried out by Sartorius CP2245 Analytical balance set and calculated by the Archimedes’ method [19].

$$P = \frac{(W-D)}{(W-S)} \times 100\%,$$

where $D$ is the weight of the sample in air, $W$ is the weight of sample with water, and $S$ is the weight of sample suspended in water.

The apparent density $D_a$ of the ceramics was measured according to the Archimedes’ formula [20]:

$$D_a = \frac{D}{(W-S)},$$

where $D$ is the weight of sample in air, $W$ is the weight of sample with water, and $S$ is the weight of sample suspended in water. The relative density $R_d$ was calculated using the formula

$$R_d = \frac{D_a}{T_d},$$

where $D_a$ is the apparent density and $T_d$ is the theoretic density of the ceramics.

2.6 Brunauer-Emmet-Teller (BET) analysis

The specific surface areas of akermanite ceramics were determined from the $N_2$ gas adsorption isotherms using Brunauer-Emmet-Teller (BET) technique on a Micromeritics ASAP-2020 surface area and porosity analyzer. BET equivalent particle size, under a spherical particle assumption, was calculated by the following equation [21].

$$D_{BET} = \frac{6 \rho}{S_{BET}},$$

where $S_{BET}$ is the specific surface area of as-milled powder ($m^2 g^{-1}$), and $\rho$ is density of akermanite (g/cm$^3$).

3. Results and discussion

3.1 X-ray diffraction (XRD) analysis

The XRD patterns of akermanite powders sintered at 1250°C is shown in Fig. 1. The sharpness of peaks shows high crystalline order of akermanite as evidenced by the highest peak at ~31.1°. The refined lattice parameter values of tetragonal akermanite were $a = b = 7.83$ Å, $c = 5.01$ Å, $\alpha = \beta = \gamma = 90^\circ$ are matched well with the standard lattice parameters ($a = b = 7.8340$ Å, $c = 5.0080$ Å, $\alpha = \beta = \gamma = 90^\circ$) which reflects the formation of akermanite (JCPDS no. 35-592). The XRD patterns of akermanite milled with 300, 400 and 500 rpm showed impurity such as diopside (CaMgSi$_2$O$_6$, JCPDS no. 41-1370).

XRD average crystallite sizes were estimated by selecting highest 6 peaks of as-milled powders. The crystallite size values for as-milled samples are listed in Table (1). According to the results obtained from Scherrer equation revealed that increasing in milling speed from 300 rpm to 500 rpm reduced the crystallite size. This is due to the increase in particle fracturing induced by high mechanical energy ball impacts and the number of impacts between material particles and milling balls collision during ball mill process [22-24]. Therefore, ball milling-mixing synthesis gradually reduces the particle sizes of the powders by activating mechanically.

| Milling speed | Average crystallite size (nm) |
|---------------|-----------------------------|
| 300 rpm, 4h   | 45.5                        |
| 400 rpm, 4h   | 44.1                        |
| 500 rpm, 4h   | 43.3                        |
Figure 1. XRD patterns of akermanite powders at different milling speeds and sintered at 1250°C

3.2 Field Emission Scanning Electron Microscopy (FESEM) analysis

The micrographs of sintered akermanite pellets at different milling speeds are illustrated in Fig. 2 (a-c). As can be seen in the FESEM images, the grain boundaries of all samples are very clear after sintering at 1250°C for 3h that indicated the sample surfaces were well crystallized. The grains are irregular in shape and non-uniform in size in all cases. The number of grain decreases as the characteristic grain size increases.

The average grain sizes of the sintered samples with milling speeds 300, 400 and 500 rpm are 1.785, 2.143 and 2.314 µm, respectively. According to the result, akermanite ceramics milled with 500 rpm sintered at 1250°C is observed with the largest grain size. This suggested that the reduction in particle size leads to the increase in particle surface area which drives overall microstructural grain growth in nanocrystalline materials. The growth of apparently larger grains is attributed by the consumption of smaller grains. Subsequently, the grain growth positively influences the densification of material ceramics [25].

Figure 2. FESEM micrographs of the sintered akermanite pellets milled with (a) 300 rpm, (b) 400 rpm, and (c) 500 rpm
3.3 Linear shrinkage measurement

The changes of the linear shrinkage of the sintered ceramics at 1250°C are described in Table 2. The values presented in the table suggest that the extent of shrinkage is mainly attributed to the specific surface area of particles. Higher specific surface area, as well as, higher surface energy can give rise to more shrinkage during the thermal treatment and consequently improved densification by reducing in porosity. I. Cristofolini et al studied the effect of sintering temperature on the shrinkage and reported that sintering leads to the progressive reduction of the total pore surface and pore volume [26]. Therefore, particle size and sintering influenced the final product dimension.

3.4 Porosity and density measurements

The apparent porosity and relative density of sintered samples with different milling speeds are listed in Table 2. Based on the result, low residual porosity could be found in all ceramic samples [27]. The sintered samples milled with 500 rpm exhibited the highest relative density in comparison with 300 and 400 rpm. This reveals that the higher milling speed produces the finer powders which could be sintered to a higher relative density [28] due to the increase in contact area between the particles. Therefore, increasing the milling speed has a good effect on relative density and apparent porosity.

Table 2. Linear shrinkage, apparent porosity and density of sintered samples at 1250°C for 3h

| Milling speed | Diameter Shrinkage (%) | Thickness Shrinkage (%) | Apparent Porosity (%) | Relative Density (%) |
|---------------|------------------------|-------------------------|-----------------------|----------------------|
| 300 rpm       | 25.465                 | 21.892                  | 3.762                 | 93.717               |
| 400 rpm       | 27.409                 | 25.459                  | 3.569                 | 96.807               |
| 500 rpm       | 27.542                 | 26.021                  | 3.485                 | 96.829               |

3.5 Brunauer-Emmet-Teller (BET) analysis

BET measurements (Table 3) revealed that the specific surface area $S_{BET}$ of as-milled powders shows an increasing trend with the milling speed, while the BET equivalent particle size $D_{BET}$ shows a decreasing trend. It means that particle size decreases because of the particle fracture induced by mechanical energy of ball impacts [29]. The highest specific surface area the finest particle size of the as-milled powders was reached to 108 m²/g at 500 rpm. This surface area result coincides again with results of XRD analysis and FESEM analysis.

Table 3. The characterization of BET specific surface area and particle size of as-milled powders

| Milling speed | BET method |
|---------------|------------|
|               | $S_{BET}$ (m²/g) | $D_{BET}$ (µm) |
| 300 rpm       | 77         | 0.026         |
| 400 rpm       | 88         | 0.023         |
| 500 rpm       | 108        | 0.019         |

4. Conclusions

Akermanite ceramics were mechanically activated by using high energy planetary ball milling and mixing. Based on the XRD results, the calculated crystallite size obtained from Scherrer method indicated that crystallite size was reduced with increasing the milling speed. According to BET analysis and SEM micrographs observation, synthesizing the starting materials by increasing milling speed produces the formation of smaller sized particles, showing the increase in the BET specific surface area of particles and leading to larger grain size due to mechanical activation and sintering temperature. The apparent porosity of sintered akermanite ceramics prepared with 500 rpm was
3.485% and relative density was 96.829%. Therefore, the results from the study showed the densest akermanite ceramics were produced at 500 rpm at sintering temperature 1250°C.

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References

[1] YJ No, JJ Li, and H Zreiqa 2017 Materials Journal 10 1
[2] P. Feng, C. Gao, C. Shuai, and S. Peng 2015 Journal of RCS Advances 5 3498
[3] E. Bernardo, J.F. Carlotti, P.M. Dias and L. Fiocco 2014 Ceramics International 40 1029
[4] C. Wu, J. Chang 2013 Biomedical Materials 8 1
[5] C. Wu, J. Chang 2006 Journal of biomaterials applications 1 12
[6] H. Gheisari Dehsheikh, E. Karamian 2016 International Journal of Bio-Inorganic Hybrid Nanomaterials 5 223
[7] Noriyuki Y. Iwata, Geun-Hyoung Lee, Yoshikazu Tokuoka, Norimichi Kawashima 2004 Colloids and Surfaces B: Biointerfaces 34 239
[8] A. Yazdani, H.R. Rezaie, H. Ghasai and M. Mahmoudian 2013 Journal of Ceramic Processing Research 14 12
[9] K. Mondal, J. Manam 2016 Journal of Molecular Structure 1125 503
[10] M. Ramezani, T. Neitzert 2012 Journal of achievements in materials and manufacturing engineering 22 797
[11] E. Karamian, H. Gheisari 2015 Nano Studies 11 87
[12] A. Kazemi, M. Abdellahi, A. Khajeh-Sharafabadi, A. Khandan, N. Ozada 2017 Materials Science and Engineering: C 71 604
[13] TP Yadav, RM Yadav, DP Singh 2012 Nanoscience and Nanotechnology 2 22
[14] H. Shin, S. Lee, H. S. Jung, J. B. Kim 2013 Ceramics International 39 8963
[15] K. Marzban 2016 Nanomedical research journal 1 79
[16] F. Tavangarian, R. Emadi, 2010 Materials Research Bulletin 45 388
[17] L. Ghorbaniana, R. Emadi, M. Razavib, H. Shinc, A. Teimourid 2012 Journal of nanostructures 357
[18] Majid Muhi Shukur, Elham Abd Al-Majeed, Mohammed M. Obeid 2014 International Journal of Engineering and Technology 4 426
[19] A. Zare-Haroftehetal, S. Saber-Samandari, S. Saber-Samandari 2016 Ceramics International 42 17781
[20] S. Ramezani, R. Emadi, M. Kharaziha, T. Tavangarian 2016 Materials Chemistry and Physics 1
[21] H. Ohsato, M. Terada, K. Kawamura 2012 Japanese Journal of Applied Physics 51 1
[22] J. Kano, F. Saito 1988 Powder Technology 98 166
[23] H. Ashrafizadeh, M. Ashrafizadeh 2012 Advanced Powder Technology 23 708
[24] M. Liu, Z. Ren, G. Chen 2013 Thermoelectric Nanomaterials, Springer Series in Materials Science 182 259
[25] I. Cristofolini, A. Rao, C. Menapace, A. Molinari 2010 Journal of Materials Processing Technology 210 1716
[26] A. L. Yurkov, T.A. Sarkisyan, D.A. Ivanov, R.C. Bradt 1997 Ceramic international 23 389
[27] Mohamed N. Rahaman 2017 Ceramic processing 9
[28] Bill Lee, Rainer Gadow, Vojislav Mitic 2017 Proceedings of the IV Advanced Ceramics and Applications Conference 140