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SINTERING BEHAVIOR OF FORSTERITE WITH MANGANESE OXIDE AS DOPING AGENT

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Abstract

Forsterite (Mg_2SiO_4) powder was synthesized using magnesium and talc with assistance of ball milling. Manganese doped forsterite was prepared at weight percentage of 0.05%, 0.1%, 0.2%, 0.5% and 1.0wt% by adding manganese oxide before ball milling. The undoped and manganese doped forsterite were sintered at temperature of 1000°C, 1100°C and 1200°C. The Vickers hardness, fracture toughness and Young's modulus have improved when 0.2wt% of MnO_2 was added in comparison with undoped forsterite. The recommended temperature to carry out the sintering process is 1100°C where improved mechanical properties were observed.

Keywords: Sintering, Forsterite, Bioceramic, Mechanical properties, Manganese oxide.

1. Introduction

Bioceramic is one of the intensely researched areas for structural replacement for humans mainly in bone tissue engineering due to their biocompability. However many works have to be done in this area due poor mechanical properties of bioceramics which hinders the usage for load-bearing applications [1]. The technology resulting from this research will enable the production of bioceramics with better mechanical properties and biocompability.

Forsterite (Mg_2SiO_4) is a bioceramic with good biocompability compared to its counterpart, hydroxyapatite. Forsterite is excellent in biomedical application especially in bone implant due to its composition which consists of magnesium and silicon which are important elements in human body. Forsterite showed good biocompatibility with better fracture toughness (K_{IC}=2.4 MPa.$m^{1/2}$) than

hydroxyapatite (0.7-1.2 MPa.$m^{1/2}$) [2, 3, 10, 11]. Forsterite also possesses melting point of 1890°C with excellent electrical insulation, thermal expansion, and chemical stability [4].

One of the critical controlling parameter that requires attention during the processing of forsterite is the selection of a suitable powder sintering method to obtain a solid, high density forsterite body that is characterized by fine-grained microstructure. The most commonly used sintering technique thus far reported in the literature is based on the conventional sintering at atmosphere pressure. This method of sintering normally requires high temperature, slow heating rate and long holding time to produce dense body, characterized by having large-grained microstructure and low mechanical properties [5]. In addition, it has been reported by Kim *et al*. [6] that nanometer sized grains and the high volume fraction of grain boundaries in nanostructured materials exhibited improved biocompatibility and osteoblast adhesion when compared to micrometer-sized grains microstructure. This shows further research is needed to determine the optimum sintering condition that can produce dense forsterite at nanostructure which improve the crystalline structure.

It has been demonstrated that nanostructure ceramics are superior in biomedical application compared to coarser crystals [7]. The study conducted by Tavangarian and Emadi [8] with nanostructure forsterite powder possessed good biocompatibility and mechanical properties which make it a suitable candidate for load bearing applications as bone implant materials. However, there were not many research work have been done on sintering process of forsterite with sintering additives to assist in lowering sintering duration and temperatures.

The research aim at synthesizing pure nanocrystalline forsterite powder and incorporating MnO_2 as sintering additive to explore the potential method in improving mechanical properties at low temperature through conventional sintering without compromising on the forsterite phase stability and inducing grain coarsening.

2. Methodology

2.1. Preparation of forsterite powder

Talc ($Mg_3Si_4O_{10}(OH)_2$, Sigma-Aldrich, 99% purity) and magnesium oxide (MgO, Merck, 97% purity) were used to prepare the forsterite powder using wet colloidal technique. The dopant used in this work was commercially available Manganese Oxide (BDH). Forsterite powders are prepared in 25g for each batch of different dopant addition (undoped forsterite, 0.05 wt% MnO_2 doped forsterite, 0.1 wt% MnO_2 doped forsterite, 0.2 wt% MnO_2 doped forsterite, 0.5 wt% MnO_2 doped forsterite, and 1.0 wt% MnO_2 doped forsterite). The forsterite powder and dopant were mixed in a 150ml of ethanol and undergo ultrasonic for 30 minutes before ball milled for 3 hours. After mixing, the wet slurry was dried, crushed and sieved into powder form. The sieved powders were pressed in uniaxial pressing machine at 30MPa to compact the powder into disc (20mm diameter, 5mm thickness) and bar (32×13×6) mm using hardened steel mould. In addition to uniaxial pressing, cold isostatic pressing (CIP) was carried out at 200MPa before sintering. The green samples were sintered in air using a rapid-heating furnace (ModulTemp)

with ramp rate of 10°C /minutes and a dwell time of 2 hours at different temperatures ranging from 1000°C, 1100°C, and 1200°C. The samples are tagged as shown in Table 1.

Table 1. Identification tag for each sample pressed.

Weight Percentage of MnO_2	Sintering Temperature					
	1000 °C		1100 °C		1200 °C	
	Disc	Bar	Disc	Bar	Disc	Bar
0	A1	A1	A2	A2	A3	A3
0.05	B1	B1	B2	B2	B3	B3
0.1	C1	C1	C2	C2	C3	C3
0.2	D1	D1	D2	D2	D3	D3
0.5	E1	E1	E2	E2	E3	E3
1.0	F1	F1	F2	F2	F3	F3

2.2. Bulk density measurement

The bulk density of the forsterite will be determined by using Archimedes method using water as medium. The bulk density was determined by precisely calculating the dry weight, suspended weight and saturated weight of forsterite. The dry weight was calculated through measurement of geometric dimension (cylindrical for disc and cube for bar) and sample mass. The suspended weight was measured in a dish submerged in water after the electronic balance (Mettler-Toledo, Switzerland) is set to zero. The saturated weight are measured immediately afterwards to get weight of water-saturated forsterite.

2.3. Young's Modulus

The Young moduli of forsterite ceramic was measured by using sonic resonance method (GrindoSonic: MK5 "Industrial", Belgium) with ASTM E1876-97 (1998) standard. First, dimensions (width, length, and thickness) of ceramic sample were measured. The sample was put into the instrument which determines the resonance frequency of the sample. Equation (1) is used to calculate the Young's modulus:

$$E = 0.9465 T_c \left(\frac{mF^2}{b}\right)\left(\frac{L}{t}\right)^3 \quad (1)$$

where E is the Young's modulus (GPa), m is the mass of bar in gram, b is the width of the bar in mm, L is the length of the bar in mm, t is the thickness of the bar in mm and Tc is the correction factor, and F is the fundamental resonance frequency of the bar in flexure in Hz.

2.4. Vickers hardness test

Vickers indentation test will be used to determine the hardness of forsterite ceramic by using standard microindentation device (Matsuzawa, Japan). ASTM E384-99 (1999) and ISO 14705 (2000) are the standards used as quality control in this test. The indentation was made using pyramidal diamond indenter with a load of 50g. The indentation was applied slowly and held for 10 seconds. The pyramidal impression left by the indenter was measured with microscope to nearest 0.1μm, thus the value of average diagonal (2a) are obtained. Equation (2) is used to determine the hardness.

$$H_v = \frac{1.845P}{(2a)^2} \tag{2}$$

where H_v is the hardness (GPa) , P is the applied load (kgf) and $2a$ is the average diagonal (μm).

2.5. Fracture toughness test

Fracture toughness test will be evaluated by using crack measurement method and using Niihara's formula shown in Eq. (3). The principle is the same as Vickers indentation test, however measurement of radial cracks from the pyramidal impression was measured by microscope to determine the fracture toughness.

$$K_{IC} = 0.203 H_v \sqrt{a} \left(\frac{c}{a}\right)^{\frac{3}{2}} \tag{3}$$

where K_{IC} is the fracture toughness in MPa $m^{1/2}$, c is the length of measured crack from the center of indentation at half of the average length of two indent diagonals (μm) and H_v is the hardness (GPa).

3. Results and Discussion

3.1. Densification

Results of all the samples' bulk density are shown in Fig. 1. The results indicated that the addition of MnO_2 has little positive effect on the densification factor. In general, the bulk densities of all the forsterite bodies increase almost linearly with respect to sintering temperatures. However, there is a limit in the amount of MnO_2 compositions as the results show decreasing trend. The undoped forsterite displayed optimum bulk density of 2.11 g/cm^3 when sintered at 1200°C. The lowest bulk density of 1.664 g/cm^3 was observed at 0.05wt% MnO_2 composition sintered at 1000°C. The lower limit for density of cortical bone is 1.7 g/cm^3 [9], which most MnO_2 doped forsterite samples have exceeded. Therefore, these compositions have the potential to be used for biomedical purpose due to its higher densification.

3.2. Fracture toughness and hardness

From Fig. 2, the addition of MnO_2 into forsterite shows no improvement in hardness until 0.2 wt% MnO_2 where the hardness sharply increase. The highest

hardness value of 1.27 GPa was observed at 0.2wt% MnO_2 doped forsterite sintered at 1000°C, however when sintered at 1100°C and 1200°C the values of hardness decrease.

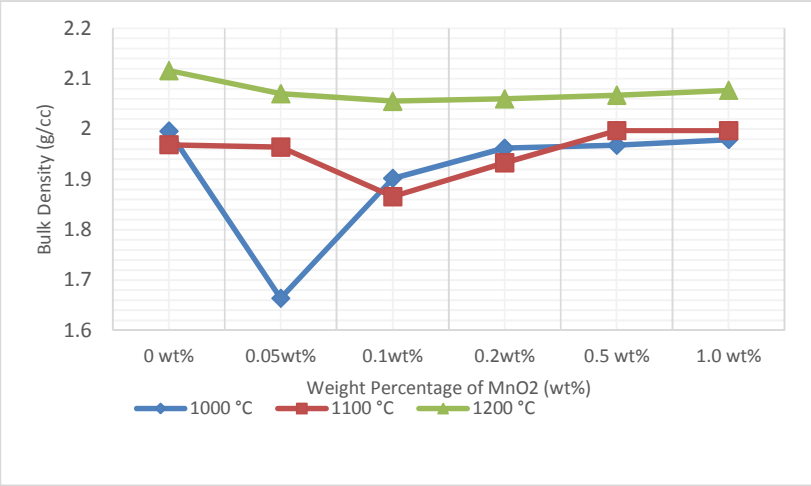

Fig. 1. Experimental data of bulk density.

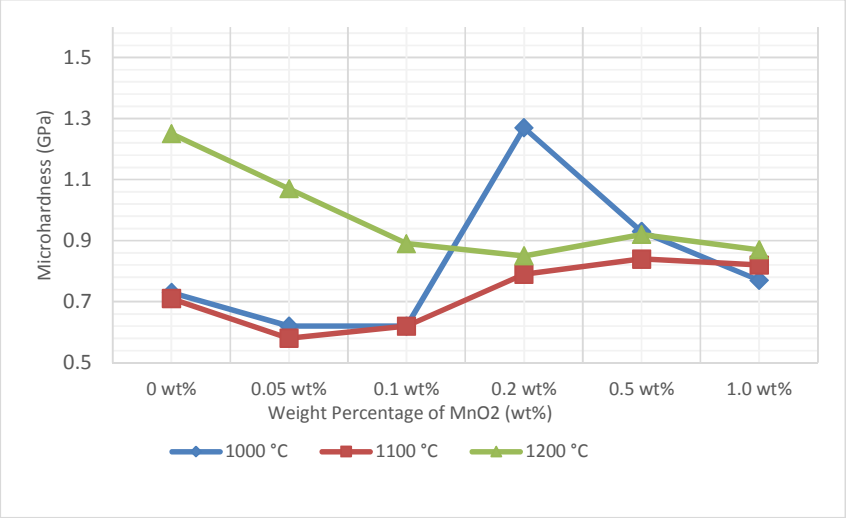

Fig. 2. Experimental data of Vicker hardness.

A similar decreasing trend in fracture toughness can be observed from Fig. 3. Forsterite sintered with 0.2wt% of MnO_2 at 1000°C showed highest fracture toughness of 1.39 MPa $m^{1/2}$ while lowest fracture toughness of 0.81 MPa $m^{1/2}$ was obtained at temperature of 1000°C with 0.05wt% MnO_2. It has been observed that the low hardness and fracture toughness values are governed by the

densification of the composition. Low bulk density samples eventually resulted to low hardness and fracture toughness values.

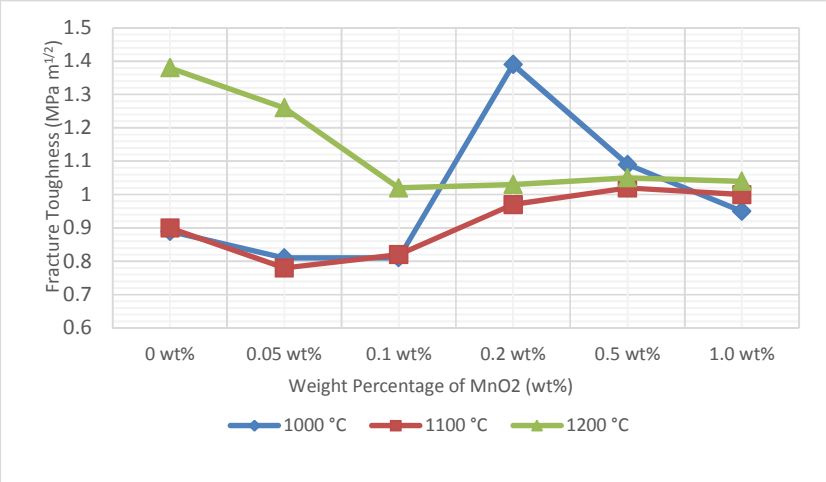

Fig. 3. Experimental data of fracture toughness.

3.3. Young's Modulus

Figure 4 below shows that on the whole, the Young's modulus increases as temperature increases. The Young's moduli show considerable amount of improvement when temperature increased from 1100°C to 1200°C. The highest value of 77GPa Young's modulus was observed at temperature of 1200°C with 0.2wt% of MnO_2.

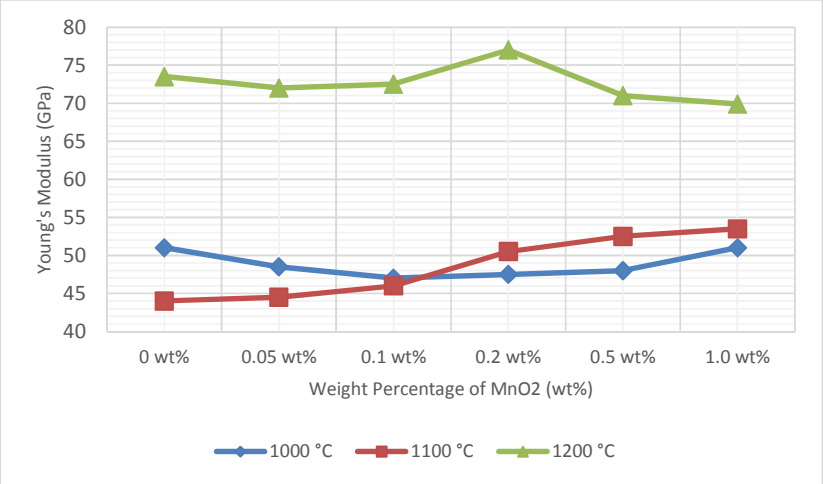

Fig. 4. Experimental data of Young's modulus.

4. Conclusions

Overall, the Vickers hardness, fracture toughness and Young's modulus have improved when 0.2wt% of MnO_2 are added in comparison with udoped forsterite. The recommended temperature to carry out the sintering process is 1100°C where improved physical and mechanical properties are observed. However these improvements of mechanical properties do not exceed the lower limit of fracture toughness and Vickers hardness for human cortical bone. Thus, the MnO_2 doped forsterite need to be improved further in term of mechanical properties before it can be used in biomedical application.

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