Effect of ZnO addition on the purity and densification of forsterite ceramic

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Abstract: Forsterite was found to the next potential candidate for bone implant application due to its superior mechanical properties as compared to the commonly used hydroxyapatite (HA). Various methods including two-step sintering and improvised synthesis method were introduced in hope to further improve the mechanical properties of forsterite. In this work, sintering additives, particularly zinc oxide (ZnO), was introduced into forsterite to provide enhancement on the densification of forsterite at lower sintering temperature. Forsterite powder was synthesized via solid-state reaction method with heat treatment at 1000 °C for 2 hours with 10 °C/min ramping rate. Addition of ZnO was conducted using milling process with composition of 0.5 wt% and 1.0 wt% ZnO. Green bulk samples were prepared prior to sintering process at 1200 °C to 1500 °C for 2 hours with 10 °C/min ramping rate. Characterization was conducted in terms of phase stability and densification of forsterite with morphology examination to observe the grain surface of all samples. It was revealed that the addition of ZnO showed a more superior densification as compared to the undoped samples at all sintering regime studied with a maximum relative density obtained at 97.7% by 0.5 wt% ZnO doped sample sintered at 1500 °C.

1. Introduction

In the context of biomedical applications, hydroxyapatite (HA) was generally popular among other bioceramics owing to its excellent biocompatibility to the human body [1,13]. Nevertheless, for many years HA was not used in load-bearing application due to its low mechanical properties, particularly fracture toughness (0.7 – 1.2 MPa m1/2) when compared to the human bone (2 – 12 MPa m1/2) [2,10]. This has motivated researchers to move towards other potential bioceramics and thus forsterite was introduced. In the early years, forsterite (Mg2SiO4) was not thoroughly investigated by researchers until recently due to the relatively high fracture toughness (2.4 MPa m1/2) and good biocompatibility [2].

Various methods were introduced in producing forsterite with enhanced mechanical properties such as solid-state reaction method, sol gel method, molten salt approach and aqueous route [3-7]. Even different sintering methods were introduced throughout the research to further enhance the mechanical properties such as spark plasma sintering [8] but most of these methods introduced were either costly or complex. Hence, sintering additives was introduced and was widely used by many researchers especially on HA, alumina and zirconia [9]. Doping with another chemical substance was known to improve the chemical and mechanical properties of bioceramics. It was reported by Mukhopadhyay...
and Basu (2007) that dopant was found to restrict possible grain growth consequently producing nano-scaled grains. However, it is possible that adding dopant into forsterite could deteriorate the thermal stability of forsterite causing the formation of secondary phases known as enstatite and periclase which is undesirable to the mechanical properties (Sarve and Hummel, 1962; Meilcarek et al., 2004).

Zinc oxide (ZnO) was known to provide positive stimulatory on the bone construction by subduing osteoclastic bone resorption (Yamaguchi, 2010; Miao et al. 2005). It was conducted by Bandyopadhyay et al. (2007) that doping ZnO on HA produced significantly higher density as compared to the undoped HA. Owing to this appealing result obtained, sintering additives in particular ZnO, was introduced into forsterite. In this work, forsterite powder was first synthesized via mechanochemical method (solid state method) with heat treatment prior to the doping of ZnO. Investigation was conducted on the thermal stability and densification rate of both undoped and doped samples.

2. Materials and methods

2.1. Synthesis of forsterite powder

Forsterite was produced via solid-state method. Two precursors were prepared (Magnesium carbonate basic; Merck, 98% and Mg3Si4O10(OH)2; Sigma-Aldrich, 99%) and mixed with a weight ratio of 1.302:1, respectively. The solvent used for the mixing is ethanol. Each precursor was subjected to ultrasonic for 2 minutes to reduce agglomeration of powders followed by another 30 minutes of ultrasonic after mixing both of the precursors together. Upon ultrasonication, milling was carried for 5 hours using attrition milling machine with 550 rpm. Zirconia balls with a diameter of 3 mm were used as a milling media with ball to powder ratio of 30:1. Prior to the completion of milling (5 mins before), 1 mol of ammonium chloride (Merck) was added into the mixture. Upon drying at 60 °C for 24 hr, the mixture was crushed and sieved using a metal mesh (212 um). As-obtained powder was then heat treated at 1000 °C for 2 hours with a ramp rate of 10 °C/min.

2.2 Doping Stage

Forsterite powder was mixed with zinc oxide (ZnO; Systerm) with weight ratio of 0.5 wt% and 1.0 wt% into a beaker filled with 200 ml ethanol, respectively. Ultrasonic vibration was conducted on the mixtures for 30 min prior to attrition milling for 1 hour at 550 rpm. Similar steps during the synthesis of forsterite powder were taken i.e. milling, drying and sieving. Upon obtaining ZnO doped forsterite powders for both compositions, uniaxial press at 2.5 MPa was done on the powder to form disc-shaped samples. Sintering at 1200 oC to 1500 oC for 2 hours with ramp rate of 10 oC/min was done on the samples. Subsequently, grinding and polishing using silicon carbide (SiC) and diamond paste was carried out prior to body characterization, respectively.

2.3 Characterization Stage

Thermal stability of forsterite was analysed via X-ray diffractometer (XRD) (Empyrean, PANalytical, Netherlands) operating at 45 kV and 40 mA via Cu-Kα radiation source. Step scan and scan speed of 0.02° min-1 and 0.5° min-1 with 2Θ scanning range from 20° to 50°. Joint Committee on Powder Diffraction Standards (JCPDS) reference cards were used to observe the stability of the samples. The lists of the cards used are as follows: forsterite (00-034-0189), periclase (00-043-1022), and enstatite (00-011-0273).

The bulk density of forsterite was measured using water immersion technique, based on Archimedes principle, with distilled water as the medium for immersion. The relative density was calculated by comparing it with the theoretical density of forsterite ($\rho = 3.271 \text{ g cm}^{-3}$) [2].
3. Results and discussions

The XRD analysis in Figure 1 showed that upon heat treatment on the milled mixture at 1000 °C for 2 hours with ramp rate of 10 °C/min, only forsterite peaks were observed. No sign of secondary phases such as enstatite and periclase was seen.

![Figure 1. Thermal stability of forsterite powder upon heat treated at 1000 °C/2 hours at 10 °C/min.](image)

As a controlling factor, Figure 2 showed the XRD result of undoped samples upon sintered at its lowest and highest sintering temperatures. Comparative study was done with both 0.5 wt% and 1.0 wt% ZnO doped forsterite samples shown in Figure 3 and 4. It was found that addition of ZnO into forsterite did not lead to any decompositions or chemical changes that could harm the overall densification of forsterite. It was reported by Tavangarian and Emadi (2009) that the presence of either periclase and/or enstatite would harm the overall mechanical performance of forsterite ceramics [12].

![Figure 2. Thermal stability of undoped forsterite bulk upon sintering at the 1200 °C and 1500 °C.](image)
In terms of densification of forsterite bulk, all samples showed an increase in density with sintering temperature. Nevertheless, ZnO doped samples showed higher relative density as compared to undoped sample with a maximum densification of 97.7% followed by 95.5% obtained by 0.5 wt% and 1.0 wt% ZnO doped sample, respectively, at 1500 °C. At sintering temperature of 1200 °C to 1300 °C, all samples showed higher rate of densification owing to the formation of grains stage. At this point, the porosities were slowly removed and grains were formed. The relative density obtained in this study is higher than the relative density reported by Ramesh et al. [11] by 7%. The effect of doping ZnO had significantly enhance the densification of forsterite and the microstructure of of the dense 0.5 wt% ZnO doped forsterite was shown in Figure 6. At 1350 °C, all the doped samples have reached its plateau as the relative density began to settle down within the range of 97-98% relative density. The relative density of undoped samples was still
The addition of ZnO into forsterite had proven to be beneficial to the densification of forsterite ceramics. With this appealing result obtained, further study can be conducted to observe on the hardness and fracture toughness of forsterite.

4. Conclusion

In conclusion, we managed to doped ZnO into forsterite without affecting the thermal stability of forsterite and producing phase-pure forsterite upon sintering at 1200 °C to 1500 °C. The highest relative density was obtained by 0.5 wt% ZnO doped sample when sintered at 1500 °C with a value of 97.7% whereas undoped sample only obtained 93.5%. The densification of ZnO doped forsterite showed promising result that could lead to enhancement not only in densification but also other mechanical properties.

Figure 5. Relative density of undoped and doped forsterite bulk with respect to sintering temperatures.

Figure 6. Morphology of 0.5 wt% ZnO doped forsterite sample sintered at 1500°C.

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