Research Paper

Nanocrystalline forsterite for biomedical applications: Synthesis, microstructure and mechanical properties


Center for Advanced Manufacturing and Materials Processing, Department of Mechanical Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia

A R T I C L E   I N F O

Article history:
Received 10 March 2013
Received in revised form 3 May 2013
Accepted 6 May 2013
Available online 22 May 2013

Keywords:
Biomaterials
Nano flakes
Fracture toughness
Synthesis
Load-bearing implants

A B S T R A C T

Forsterite (Mg2SiO4) because of its exceptionally high fracture toughness which is close to that of cortical bones has been nominated as a possible successor to calcium phosphate bioceramics. Recent in vitro studies also suggest that forsterite possesses good bioactivity and promotes osteoblast proliferation as well as adhesion. However studies on preparation and sinterability of nanocrystalline forsterite remain scarce. In this work, we use a solid-state reaction with magnesium oxide (MgO) and talc (Mg3Si4(OH)2) as the starting precursors to synthesize forsterite. A systematic investigation was carried out to elucidate the effect of preparatory procedures including heat treatment, mixing methods and sintering temperature on development of microstructures as well as the mechanical properties of the sintered forsterite body.

1. Introduction

Poor adhesion of biomimetic hydroxyapatite coatings to metal implants (Zheng et al., 2000) which can lead to wear debris-induced osteolysis (Amstutz et al., 1992) has sparked interest in realization of full bioceramic prostheses; yet low fracture toughness of calcium phosphates (Ruys et al., 1995) poses a considerable challenge to development of load-bearing implants. While a number of studies have previously tried to mitigate this problem by incorporation of different additives, the improved mechanical properties have never been reported to match those of natural bone (Ryu et al., 2004; Lopes et al., 1999; Kong et al., 2004). Forsterite on the other hand as a potential biomaterial for prosthetic implants exhibit a considerably higher fracture toughness compared to its close relative, enstatite (MgSiO3) which has also been reported to show good biocompatibility (Dubois et al., 1998; Goeuriot et al., 1998).

Elimination of secondary phases and hence superior mechanical properties in forsterite although depend largely on the attributes of as-synthesized crystals (Kharaziha and Fathi, 2010). Because of compositional similarities to intermediate states including enstatite, forsterite is usually synthesized via powder processing followed by long heat treatment cycles. As standard pressureless sintering requires high temperature, slow heating rate and long holding time to achieve a dense body, the process of consolidation normally produces large-grained microstructures and consequently poor mechanical properties (Ni et al., 2007). This adverse effect can be attributed to the fact that grain growth and densification occur simultaneously only as long as the intergranular pores are eliminated through diffusion. Once a few grains start to grow abnormally fast by consuming small
matrix grains surrounding them, pores get trapped within or between the excessively large grains and thus further densification becomes practically impossible. Here we try to address these issues by investigating how different approaches in preparing the initial powder influence phase stability, sinterability, microstructure and mechanical properties of the samples.

2. Material and methods

2.1. Synthesis of forsterite

Forsterite powder was prepared through a solid-state reaction using magnesium oxide (MgO; Merck, 97%) and talc (Mg₃Si₄(OH)₂; Sigma-Aldrich, 99%) as the starting precursors. The talc powder was mixed with the MgO powder at a weight ratio of 1.88:1 according to the stoichiometric composition of forsterite. The mixture was subsequently subjected to 2 min of sonication at high frequency to ensure homogeneous mixing.

Two different preparatory procedures were employed to study the development of microstructures in forsterite samples. In one case mechanical activation via sonication and ball milling for different durations was followed by heat treatment at various temperatures with a ramp rate of 10°C/min. In another case the samples were prepared under the same conditions but no heat treatment was performed before sintering. After preparation the sieved powders were uniaxially pressed at 2.5–3.0 MPa followed by another round of compaction at 200 MPa using a cold isostatic press (CIP). The pressed green samples were then sintered at different temperatures (1200°C, 1300°C, 1400°C and 1500°C). A ramp rate of 10°C/min with a dwell time of 2 h was used for all cases. The sintered samples were finally ground and polished prior to body characterization.

2.2. Microstructure and grain size

The sintered samples were thermally etched at 50°C below the sintering temperature with 10°C/min heating rate and 30 min holding time to delineate the grain boundaries.

A Zeiss AURIGA field emission scanning electron microscope (FESEM) was used to evaluate the microstructure of forsterite samples at an accelerating voltage of 1 kV in order to minimize charging effect. To measure grain size from the FESEM micrographs, the standard line intercept method (ASTM E112-96, 2004) was applied from which the average grain size D was calculated based on the equation $D = \frac{L}{C}$, where $L = C/MN$ is the average interception length, C is the total length of the test line, M is the magnification of FESEM micrograph and N is the number of intercepts (Mendelson, 1969).

2.3. Phase stability, relative density and mechanical properties

Phase stability of samples was studied using XRD (Geiger-Flex, Rigaku Japan). Young’s Moduli were determined via sonic resonance method (GrindoSonic: MKS “Industrial”, Belgium) while Vickers hardness and fracture toughness tests were performed on a standard microindentation device (Matsuzawa, Japan). Finally relative density of samples was measured using water immersion technique (Mettler Toledo, Switzerland).

3. Results and discussion

3.1. Phase stability

Homogeneous mixtures of the starting precursors mechanically activated through sonication or ball milling often possess desirable attributes in suppression of secondary phases. From the XRD data presented in Fig. 1, it can be clearly inferred that the violent nature of cavitation at high amplitudes can considerably lower the persistence of intermediate phases such as enstatite while the initial MgO precursor appears to have a more sustained yet weakened fingerprint after sonication. With direct ultrasonication at 50% amplitude, it was found that the concentration of enstatite radically decreased from 29.2% to 15.3% while for MgO only a minute decrease of 2% was observed. The relative intensities were calculated based on the highest intensity of forsterite peaks in each case.

In addition to reducing the amount of secondary phases, higher amplitude of ultrasonication were also found to improve the crystallinity of the as-synthesized forsterite powders. However in general, formation of forsterite through mechnanochemical routes alone whether by sonication or ball milling is relatively limited and the resulting nanostructures even though show remarkable transformation in morphology before heat treatment, contain pronounced quantities of initial reactants. The XRD profile of the samples after mechanical activation can be viewed in the appendices.

![Fig. 1](image-url)
While prolonged ball milling due to its far larger cascading motion suppresses the prominent MgO peak at ~43° more effectively, it has been previously reported that samples regardless of preparation method must undergo heat treatment at 1200 °C before any appreciable amount of crystalline forsterite can be obtained (Ni et al., 2007). Our results on the other hand indicate that even though an abrupt drop in concentration of secondary phases occurs beyond 1250 °C, small amounts of MgO in the samples are inevitable even after heat treatment at 1500 °C beyond which melting takes place. In particular at 1250 °C, the prominent MgO peak reduced from 18.8% to 7% while enstatite peaks dropped from 12.9% to 5.2%. These numbers evidently suggest that heat treatment temperature plays a bigger role in governing the reduction of secondary phases compared to mechanical activation, although as depicted in Fig. 2, samples ball milled for 3 h prior to heat treatment exhibit a substantial reduction (up to 18.3%) in MgO content which is a great improvement over the long ball milling times reported earlier (Ni et al., 2007; Fathi and Kharaiziha, 2009a).

The remnants of secondary phases beyond 1250 °C may be minor, but even the smallest concentrations are not favorable as they can potentially prevent complete densification and eventually deteriorate the mechanical properties. By 1300 °C for instance, enstatite peaks fully disappear and the intensity of MgO peak decrease by several orders suggesting a large boost in reaction rate of intermediate states toward the complete formation of forsterite.

A 1 h long heat treatment at 1400 °C was found to give the best result with forsterite and negligible amounts of MgO as the only detectable phases (see Fig. 3). Despite slightly better densification rates at higher temperature may, the optimum temperature used here for sintering the samples is well below the melting point of enstatite at 1557 °C (Boyd et al., 1964) and therefore adverse effects associated with phase separation of intermediate states through melting can be avoided. Longer holding times even though may produce similarly dense samples at lower temperatures, lead to reappearance of intense MgO peaks possibly due to decomposition.

It has to be emphasized that in general sintering behavior and phase stability of forsterite can vary greatly depending on the starting precursors used. In the reaction of magnesium carbonate (MgCO₃) and talc for example, it has been reported that a complete forsterite phase can be obtained only after ball milling for 10 h and heat treatment at 1000 °C for 10 min (Tavangarian et al., 2010). The results presented herein therefore are very encouraging since the ball milling time required for formation of forsterite was remarkably shortened in comparison to those reported in previous studies.

Lower temperature and shorter holding time during heat treatment as we have demonstrated here can also avoid nucleation of large crystals and consequently growth of abnormal grains. An increase in heat treatment temperature from 1200 °C to 1400 °C showed a slight rise in average crystallite size from 36.7 nm to 42.5 nm for 1 h holding time. The relative size of the crystals prepared in this manner is considerably smaller than those reported for the same temperatures in the works of Tavangarian et al. (2010).

3.2. Morphology

The mixing procedure in addition to eliminating the secondary phases largely influences the morphology of forsterite samples. As shown in Fig. 4 the powders prepared via ball milling have a coarse lamellar structure with frequent non-uniformities similar to that of the initial talc powder whereas the sonicated samples end up as very homogenous

---

Fig. 2 – The effect of prolonged ball milling on elimination of secondary phases. XRD profile of the samples after ball milling for 1 and 3 h and subsequently heat treatment at 1200 °C for 2 h.

Fig. 3 – The effect of heat treatment on phase stability of forsterite samples. The samples were ball milled for 3 h and subsequently heat treated for 1 h at different temperatures. The prominent MgO peak never fully disappears, but has a minimal intensity at 1400 °C.
nano flakes. This sharp transformation in morphology hints at formation of proto-forsterite via mechanochemical reaction which is also anticipated from XRD profiles before heat treatment (see the Appendix). Upon heat treatment the nanoflakes further crystallize and grains each a few tens to hundreds of nanometer start to emerge on their surface. The samples which have been ultrasonicated show relatively better stability in morphology, while the nanoflakes in the case of ball milled samples aggregate into multi-layer structures. The single-layer nanoflakes owing to their large surface area may not only have superior adhesion as in biomimetic coating of implants, but also enable other novel applications in drug delivery and tissue engineering.

3.3. Grain size, densification and mechanical properties

Sinterability as well as mechanical properties can both be affected by heat treatment of powders before sintering. Non-heat-treated samples surprisingly showed no signs of secondary phases upon sintering at 1300 °C, whereas the MgO peak in heat-treated samples disappeared only after sintering at 1500 °C. In spite of the fact that forsterite samples generally shrunk with increasing temperature, non-heat-treated samples once again exhibited a superior densification behavior shrinking gradually by 6.3% to 14.2% with increasing temperature whereas heat-treated samples shrunk only by 0.6% to 8.5% at the same temperatures. Shrinkage rates were significantly higher between 1400 °C and 1500 °C and 1200 °C and 1300 °C for heat-treated and non-heat-treated samples respectively which is consistent with the fact that MgO peaks normally get weaker in intensity within these intervals for each case. The values for shrinkage were also correlated with the relative densities calculated according to the theoretical density of forsterite (3.221 g/cm³) (Ghomi et al., 2011). Maximum densities of 74.4% and 90.7% were obtained for heat-treated and non-heat-treated samples respectively at 1500 °C. Hence forsterite samples sintered without prior heat treatment attained densities significantly better than previous works wherein either poor densification behavior or similar values only after very long sintering times have been reported (Ni et al., 2007; Mustafa et al., 2002).

Increase in relative density which itself is proportional to the sintering temperature improves the Vickers hardness however the hardness of non-heat-treated samples increased sharply from 2.3 GPa at 1200 °C to 7.7 GPa at the sintering temperature of 1500 °C. In contrast, the Vickers hardness

Fig. 4 – The effect of different preparatory procedures on morphology of forsterite samples. (a and b) show what is possibly a proto-forsterite sample with large amounts of MgO. These have been prepared via ball milling and ultrasonication respectively. (c and d) show the same samples after heat treatment. Crystallization and growth of grain on the surface are evident. The sample which was prepared by sonicated retained its single-layer flake-like structure while the other has undergone a change in morphology to produce multi-layer lamellar structures.
values obtained for heat-treated samples even at high sintering temperatures were not favorable (<1.7 GPa). These results indicate that the value of hardness is governed by preparatory procedures which in turn eliminate secondary phases and improve the bulk density of the sintered body.

The trend of fracture toughness is also similar to the pattern acquired from Vickers hardness as a function of sintering temperature. Heat treated samples show considerably inferior values for toughness, but as calculated from Niihara’s equation, the highest fracture toughness (5.16 MPa m$^{1/2}$) achieved for non-heat-treated forsterite in this study is 115% greater than that prepared using sol–gel (Ni et al., 2007) and 20% higher than the results obtained by two step sintering (Fathi and Kharaziha, 2009b). This value readily surpasses the lower limit of cortical bone (2 MPa m$^{1/2}$) and therefore makes nanocrystalline forsterite a good candidate for biomedical applications (Hench, 2005).

Elastic properties of the samples were studied using the dynamic resonance method. In heat-treated samples, the Young’s modulus was found to be directly proportional to the grain size which only slightly changes with increasing sintering temperature. A sharp increment occurred between 1400 °C and 1500 °C where a maximum stiffness of 89.7 GPa was obtained. In non-heat-treated samples on the other hand, Young’s modulus increased with density and sintering temperatures only until 1300 °C (77.7 GPa), but a further increase in sintering temperature (1300–1500 °C), which for this case caused a large growth in grain size, in turn led to deterioration of Young’s modulus down to 11.5 GPa. It can be postulated that while fracture and hardness in forsterite are related to density, stiffness is largely governed by a reverse Hall–Petch relationship until a critical grain size which varies depending on the preparation methods. In heat-treated samples it appears that migration of MgO to the surface of crystals effectively suppresses grain growth during sintering as evident from Fig. 5. However MgO concentrations at the grain boundaries obstruct a complete densification simultaneously and thus other desirable attributes such as high hardness and fracture toughness decline. As suggested by data represented in Fig. 6 the critical grain size for non-heat-treated samples is ~1.6 μm after which densification slows down as the grains grow larger. On the contrary heat-treated samples before an average grain size of ~1.1 μm follow a reverse Hall–Petch relationship. This idea is consistent with our recent findings that MgO beyond 1% caused pronounced porosity at the grain boundaries in hydroxyapatite samples deteriorating their Young’s moduli while enhancing their fracture toughness and hardness (Tan et al., in press).

4. Conclusions

The effect of preparation methods on microstructure and mechanical properties of forsterite was studied. Morphology of proto-forsterite nanoflakes synthesized through the solid-state reaction of magnesium oxide and talc was found to be directly governed by the method of mechanical activation. In particular samples prepared via ultrasonication exhibited uniform and single-layer structures while once ball milled the morphology transformed into multi-layer lamellar structures despite having considerably lower amounts of secondary phases compared to the former case. Heat treatment was also demonstrated to be an important factor in elimination of MgO and enstatite, however small amounts of MgO appear to be inevitable even at high sintering temperatures, i.e. 1500 °C. The forsterite samples which were heat-treated before sintering had poor Vickers hardness and fracture toughness while having a superior Young’s modulus. It was concluded that heat treatment results in migration of MgO contents to the surface of the crystals where they suppress grain growth.

![Fig. 5 – Grain size and densification behavior at various sintering temperatures. (a, b, c and d) demonstrate sinterability of heat-treated samples at sintering temperatures of 1200 °C, 1300 °C, 1400 °C and 1500 °C respectively. (e, f, g and h) are sintered samples of non-heat-treated forsterite powders at the same sintering temperatures. It is evident that the heat treated samples retain smaller grain size but do not consolidate completely even at high temperatures. For non-heat-treated samples on the other hand grain growth and densification with increasing temperature are very significant.](image-url)
during sintering but simultaneously obstruct densification. On the other hand a reverse Hall–Petch relationship were proved to hold for non-heat-treated samples before the average grain size reaches ~1.6 µm beyond which the Young’s modulus drop steeply. Non-heat-treated samples also have significantly better hardness and fracture toughness which can be attributed to their high relative density and lower concentration of MgO contents.

Cold-pressed green bodies of nanocrystalline forsterite upon sintering exhibit superior mechanical properties which in turn enable machining of dense cylinders into a variety of geometries, spiral as in screw-retained prostheses or otherwise. Therefore with regard to mechanical properties, nanocrystalline forsterite prepared through optimal routes appears to be a good successor to calcium phosphate bioceramics especially for load bearing applications.

Furthermore nano flakes owing to their exceptional morphology may enhance adhesion of biomimetic coatings on implants of metallic nature when applied as successive thin films however the problem of hydrophobic interactions in colloidal solutions can be problematic for non-functionalized nanostructures deposited via techniques such as electrophoretic deposition (EPD). Along with this issue, concerns over biodegradation as well as osteoblast proliferation of this novel material are currently being studied both in vitro and in vivo and the results will be reported in subsequent works shortly.

Acknowledgments

This study was supported under the HIR Grant No. H-16001-00-D000027. The authors gratefully acknowledge the Ministry of Higher Education Malaysia for the financial support.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jmbbm.2013.05.008.

References


Fig. 6 – Grain size, relative density and mechanical properties versus sintering temperature for non-heat-treated (dashed lines) and heat-treated (solid lines) samples. It is clear that beyond a critical size, ~1.6 µm for the non-heat-treated samples, Hall–Petch relationship effectively applies while for heat-treated samples beyond a critical grain size of ~1.1 µm a reverse Hall–Petch relationship is observed. In contrast Vickers hardness and fracture toughness appear to be solely proportional to relative density.


