



Original Research Paper

Formation mechanism of nano-hardystonite powder prepared by mechanochemical synthesis



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ABSTRACT

Hardystonite is currently recognized as a biocompatible bio-ceramic material for a range of medical applications. In this study, pure nano-crystalline hardystonite powder was prepared by mechanochemical synthesis of calcium carbonate, zinc oxide and silicate oxide in a planetary ball mill followed by sintering. A range of techniques including X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were applied to fully characterize the obtained powders. The effect of time and sintering temperature on the formation mechanism of nano-hardystonite was studied. It was found that pure nano-crystalline hardystonite powder formation occurred following 20 h of milling and subsequent sintering at 900 °C for 3 h. The measured crystallite and agglomerate particle size were found to be 28 ± 2 and 191 ± 3 nm, respectively. The two-step sintering processing was also applied for the preparation of bulk hardystonite. The compressive strength and elastic modulus of bulk hardystonite with $75.5 \pm 3\%$ relative density were approximately 121 ± 2 MPa and 27 ± 4 GPa, respectively.

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1. Introduction

Ceramic is a non-metallic, inorganic material that have a wide range of applications in aerospace, refinery, chemical industries, electronics, optics and healthcare [1,2]. Amongst these applications, much interest has been devoted to the use of ceramics and glasses in biomedical applications including soft and hard tissue replacement and regeneration [3]. The great potential applications of bio-ceramics are due to their high biocompatibility, bioactivity, easy fabrication and high stiffness [4]. However, regardless of their suitable biological properties, the inherent brittle nature of this class of material limits their application in medicine [5]. Often, bio-ceramics are used with polymeric matrix to produce bio-composites [6] or are coated on the surface of implants to enhance tissue-material interactions *in vivo* [7].

Hydroxyapatite is an example of a bio-ceramic that has been in use for the past few decades as bone substituted material [8]. However, the weak mechanical properties (unsuitable elastic modulus, low fracture toughness and brittle behavior) and the low degradation rate of hydroxyapatite in biological environment limits their use in tissue engineering applications [9]. Recently, Calcium silicates (e.g. CaSiO_3) have received great attention as an alternative

bio-ceramic for hard tissue engineering due to their enhanced mechanical properties compared to hydroxyapatite [10]. However, calcium silicates are known to have a high degradation rate in physiological environment, leading to an increase in the local pH of the surrounding tissue, hence resulting in tissue damage [11].

The addition of elements such as Zn, Mg and Zr as network modifier into calcium silicate network can improve the dissolution and degradation rate [12]. Previous studies on hardystonite ($\text{Ca}_2\text{-ZnSi}_2\text{O}_7$) have demonstrated good mechanical [13] and biological properties. The mechanical properties of hardystonite, such as bending strength (136 MPa), fracture toughness ($1.24 \text{ MPa m}^{1/2}$) and Young's modulus (37 GPa) are close to that of bone [13]. This is considered advantageous since for bone tissue replacement and regeneration the stress-shielding phenomenon, which may occur due to the difference mechanical properties of replaced material with natural tissue, can be negligible [14]. In addition, hardystonite possess enhanced chemical stability, in physiological environment, compared to calcium silicates [15]. The release of Zn from hardystonite network has shown to have anti-inflammatory and anti-bacterial properties [16].

To broaden the medical applications of hardystonite, Wang et al. [17] reported the fabrication of hardystonite-wollastonite scaffolds with a higher compressive strength and lower degradation rate compared to pure wollastonite scaffolds. In another study, hardystonite was successfully coated on Ti-6Al-4V substrate by

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plasma spraying method and an improved cell attachment, proliferation and differentiation were observed [18]. Zeriqaq et al. [19] reported that the incorporation of Zn and Sr in calcium silicate ceramics could improve bone tissue regeneration and integration when tested in rat tibia *in vivo*.

Wu et al. [13] produced hardystonite powder through sol-gel synthesis route and applied a high sintering temperature (1200 °C) during the processing, which resulted in irregular, agglomerated and large (5–40 μm) particles. Therefore, a reduction in sintering temperature is a step to achieve nanostructures with enhanced surface properties. Recently, mechanochemical synthesis has proven to be an effective and economical method for nanostructure and nano-crystalline ceramic fabrications. In this method, surface of the reactants are mechanically activated and so a lower processing temperature is often required [20]. The main objective of this study was to obtain pure nano-hardystonite by mechanochemical synthesis and subsequent sintering. Phase evaluation during processing and the chemical reactions of nano-hardystonite formation are also studied. The effects of ball milling time and sintering temperature on the formation mechanism of nano-hardystonite are also evaluated. In addition, the two-step sintering method is applied for the first time to prepare bulk nano-hardystonite ceramics.

2. Materials and methods

2.1. Powder preparation by MA method

In this research, hardystonite powder was prepared by mechanochemical synthesis. zinc oxide (ZnO, 99% purity, Merck), calcium carbonate (CaCO₃, 98% purity, Merck) and silicate oxide (SiO₂, 99% purity, Aldrich) powders, with a molar ratio of 1:2:2 respectively, were mixed in a planetary ball mill (Retsch, PM 100) in zirconia vial containing five zirconia balls of 20 mm in diameter. The ball/powder mass ratio was 10:1 and the rotational speed of the disc and vial was set at 250 and 500 rpm, respectively. The time of milling was chosen at 5 min and 2 h, 5 h, 10 h, 20 h followed by sintering at 900 °C, 1000 °C and 1100 °C for 3 h. The complete details of each sample are presented in Table 1.

2.2. Particle characterization

Phase transformation evaluations for the powders prepared by mechanochemical synthesis at different time and sintering temperature were studied using X-ray diffraction (XRD) (X'pert

Philips) equipped with Cu K α radiation ($\lambda = 0.154$ nm at 40 kV and 30 mA). Data were collected over the 2θ range of 20–70° by scan rate of 0.05° per second. The crystallite size was measured by Scherrer equation (Eq. (1)). Three peaks with high intensity were selected for calculation of crystallite sizes of powder after subsequent sintering [21].

$$\beta \cos \theta = \frac{k\lambda}{D} \quad (1)$$

where θ is the Bragg diffraction angle, D is the crystallite size, λ is the wavelength of the X-ray radiation, β is the diffraction peak width at half maximum intensity and K is a constant related to crystallite shape, normally taken as 0.9.

Particle size and morphology were studied by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) using Philips EM208S with 100 kV operating voltage and Philips XL30 was working by acceleration voltage of 30 kV, respectively. The particle sizes of milled powders were estimated from both TEM and SEM images by using Image analysis software (image J).

The milled powders were uniaxial pressed into pellets of 12 mm \times 18 mm under pressure of 600 MPa. The samples were then sintered at 1100 °C for 30 min and 900 °C for 13 h, respectively. The compressive strength and elastic modulus were measured by Hounsfield (H25KS).

In this study, the liner shrinkage of hardystonite and its relative density (by Archimedes technique) were evaluated according to the following equations:

$$\text{Liner Shrinkage} = \frac{L_g - L_s}{L_g} \quad (2)$$

$$\text{Relative density} = \frac{\rho_m}{\rho_t} \quad (3)$$

where L_g is the bulk length before sintering, L_s is the bulk length after sintering, ρ_m is the measured density and ρ_t is the theoretical density. Five consequent samples were used for each mechanical and physical test.

3. Results and discussion

3.1. X-ray diffraction evaluation and reaction mechanism

Fig. 1 represents the XRD pattern of H₁–H₅ samples. Fig. 1 (H₁) shows the XRD patterns for the raw materials, which are consistent with the standards for CaCO₃ (XRD data file No. 5-0586), SiO₂ (XRD data file No. 46-1045) and ZnO (XRD data file No. 1-075-0576) compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS). Milling for 20 h (H₅) has led to a broadening of the XRD peaks and a significant decrease in their intensities because of the internal strain and the formation of nano-crystalline materials during Mechanochemical synthesis. Also this phenomenon can be due to gradual transfer of the raw materials to amorphous state. According to Fig. 1 new crystallite phase at various milling time was not detected. Hence it can be suggested that hardystonite and other intermediate phases are unable to form just by applying mechanochemical method.

The XRD patterns for H₆–H₁₀ samples are presented in Fig. 2. All the samples were sintered at 900 °C.

The XRD pattern for sample after 5 min ball mill followed by sintering at 900 °C is presented in Fig. 2 (H₆) where sharp peaks for CaO (XRD JCPDS data file No. 17-0912) are detected. Le and Oh [22] suggested that completion of reaction (4) occurs at 800 °C. Results presented in Figs. 1 (H₁) and 2 (H₆) suggest that the first step of hardystonite formation might have occurred based on the following Eq. (4):

Table 1
Sample conditions for mechanochemical method.

Samples	Temperature (°C)	MA time (h)
H ₁	–	5 min
H ₂	–	2
H ₃	–	5
H ₄	–	10
H ₅	–	20
H ₆	900	5 min
H ₇	900	2
H ₈	900	5
H ₉	900	10
H ₁₀	900	20
H ₁₁	1000	5 min
H ₁₂	1000	2
H ₁₃	1000	5
H ₁₄	1000	10
H ₁₅	1000	20
H ₁₆	1100	10
H ₁₇	1100	20

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