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ScienceDirect

Procedia Materials Science 5 (2014) 212 – 221

Procedia Materials Science

www.elsevier.com/locate/procedia

International Conference on Advances in Manufacturing and Materials Engineering, AMME 2014

Estimation of Crystallite Size, Lattice Strain and Dislocation Density of Nanocrystalline Carbonate Substituted Hydroxyapatite by X-ray Peak Variance Analysis

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Abstract

X-ray peakprofile analysis by variance method is employed to evaluate the micro structural parameters namely crystallite size, mean squared lattice strain, root mean squared lattice strain and dislocation density of hydroxyapatite (HA) and carbonate substituted [3 wt% (3CHA) and 6 wt% (6CHA)] hydroxyapatite nanoparticles prepared by microwave synthesis technique. The calculated average crystallite sizes of HA, 3CHA and 6CHA by variance method are correlated with the values obtained from Scherer's and transmission electron microscopy (TEM) results. It is found that the results of the average crystallite size measured by variance analysis method are in good agreement with TEM results. The calculated micro structural parameters are also correlated with the *in-vitro* dissolution study results. It is found that variance method of X-ray peak profile analysis is more appropriate to quantify the micro structural parameters of nanostructured hydroxyapatite based nanoparticles.

Selection and peer-review under responsibility of Organizing Committee of AMME 2014

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Selection and peer-review under responsibility of Organizing Committee of AMME 2014
doi:10.1016/j.mspro.2014.07.260

*Keywords:*Hydroxyapatite; Carbonate; Nanosize; Dissolution; XRD; TEM.

1. Introduction

Hydroxyapatite [HA, $Ca_{10}(PO_4)_6(OH)_2$] has been extensively used as a biomaterial in bone grafting, bone tissue engineering, and bone drug delivery due to its excellent properties of biocompatibility, bioactivity, osteoconductivity, non-toxicity, non inflammatoriness and non-immunogenicity. Although HA is considered as a good bone substitute, it is the least soluble and the most stable material among the calcium phosphates, which is an undesirable characteristic because it may impede the rate of bone regeneration upon implantation. It is always desirable that a bone substitute should be bioresorbable to some extent so that it can be replaced with the regenerated bone over a period of time. The resorbability of HA can be improved with the help of some ionic doping agents or by reducing its grain size to the nano level (Murugan and Ramakrishna, 2003). It was shown that the substitution of CO_3^{2-} into the apatite structure improves the resorbability of HA. The carbonate ions, which can occupy about 3-8 wt% of the calcified tissues, can be substituted either for the phosphate ion (B-type substitution) or for the hydroxyl ion (A-type substitution) or for both the ions (AB-type substitution) in the apatite lattice. The B-type substitution of CO_3^{2-} leads to a decrease of a-axis and an increase of the c-axis of the HA lattice (LeGeros, 1965; LeGeros et al., 1967). The presence of B-type CO_3^{2-} in the apatite lattice was shown to cause an increase in solubility both *in-vitro* and *in-vivo* tests (Krajewski et al., 2005). Hence, among the variety of HA-based ceramics, carbonated HA (CHA) appears to be an excellent material for bioresorbable bone substitutes (Suchaneka et al., 2002)

Nanocrystalline HA-based ceramics such as nano CHA is expected to have homogeneous resorption and better bioactivity than coarser crystals (Webster et al., 2001). The properties and the performance of HA based bioceramics can be improved by changing powder particle size and shape, their distribution and agglomeration (Best and Bonfield, 1994). Apart from this, it was recently reported that nanosized CHA crystals with low crystallinity could be successfully applied to fabricate CHA/collagen biodegradable composites and when these composite materials were implanted in rabbits, they underwent resorption and promoted new bone formation (Du et al., 1998). Therefore, synthesis of CHA powders with desired properties such as nano size, low crystallinity, controlled morphology and chemical composition is of great importance.

Many researchers [LeGeros et al., 1967; Lafon et al., 2003; Pan and Darvel, 2010] have reported various methods of preparation of carbonated HA and studied the effect of carbonate substitution on lattice parameters, morphology, thermal decomposition and solubility of HA. In addition a few researchers (Krajewski et al., 2005) have studied the various types (A, B and AB) of CO_3^{2-} substitution and the various quantification methods of CO_3^{2-} in HA lattice. But a certain gap exists in the literature in estimating and correlating the micro structural parameters such as the accurate crystallite size, the mean squared lattice strain, the root mean squared lattice strain and the dislocation density to the structural and the dissolution properties of CHA, which might provide the information for better understanding of the differences in dissolution properties of CHA compared to the HA.

For better correlation of the nanoscale material properties to their above mentioned micro structural parameters thereby achieving proper understanding and prediction, their size is required to be calculated as accurately as possible. So far, Scherrer method is a well known method to calculate the crystallite size based on the broadening of the X-ray diffraction peaks from the powder diffraction data. However, Scherrer method underestimates the crystallite size because of not considering the instrumental and strain contribution to the X-ray diffraction peak broadening. Hence X-ray diffraction peak profile analysis has been widely used to calculate the crystallite size more accurately by considering all the other important factors such as instrumental and strain contribution to the X-ray diffraction peak broadening. Apart from these, the various analytical methods such as the whole diffraction pattern fitting methods are also being used to estimate the crystallite size and the lattice strain present in the material from X-ray peak broadening (Warren and Averbach, 1950). However, fitting the complete powder diffraction data accurately is complicated and hence it attracts many indirect methods such as Williamson-Hall (W-H) method and Warren- Averbach (W-A) analysis for estimating the lattice strain and crystallite size [Warren et al., 1951;