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Mechanical properties of tricalcium phosphate single crystals grown by molten salt synthesis

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Abstract

Mechanical properties of flux-grown tricalcium phosphate (TCP) single crystals ranging in size from 50 to 75 μm have been characterized by performing micro- and nanoindentation on their facets. Notwithstanding the inherent brittleness and anisotropy, these single crystals exhibit nanoscale plasticity in the form of pile-up around the edges of indents. A similar plastic response was observed in hydroxyapatite (HA) single crystals during nanoindentation in an earlier study. The hardness and elastic modulus obtained during nanoindentation are discussed in comparison with the polycrystalline forms of both TCP and HA found in the literature. The indentation fracture toughness values of TCP single crystals were found to be higher than those of HA single crystals. The higher values are attributed not only to the difference in crystal structure and corresponding differences in surface energy, but also to extensive crack bridging by ligament formation across crack faces during crack propagation.

Keywords: Single crystals; Tricalcium phosphate; Plasticity; Crack bridging; Nanoindentation

1. Introduction

Calcium phosphates exhibit excellent biocompatibility, bioactivity and biodegradability in bone replacements, thus it is important to understand the mechanical responses of artificially grown calcium phosphate ceramics [1]. Of these ceramics, hydroxyapatite (HA) and tricalcium phosphate (TCP) are the materials that have been most investigated for the purpose of medical implants, bone defect fillers and bone tissue engineering [2,3]. TCP crystals are preferred over HA due to their excellent resorbability [4], which allows their dissolution in the surrounding body fluid and eventual replacement by body tissues. Biphasic composites, which are mixtures of HA and β-TCP, provide an optimum dissolution rate and other advantages for better performance [5–7]. However, the biphasic composites cannot be used for load-bearing applications due to their poor mechanical properties. There have been several attempts to enhance the mechanical properties of porous biphasic scaffolds to enable their use in bone tissue engineering [8]. Though the mechanical properties of HA and TCP in polycrystalline form have been studied extensively [9–12], it is important to determine the mechanical properties of the corresponding single crystals. Recently, while studying the anisotropic mechanical properties of HA single crystals, it was shown that HA exhibits nanoscale plasticity [13]. To the best of our knowledge, the deformation and fracture of single crystalline TCP have not been studied, possibly due to the difficulty in processing TCP single crystals of workable sizes. Thus, the present work assumes significance not only for understanding the mechanical behavior of artificially grown single crystals but also for providing insights into the development of HA and β-TCP biphasic composites with good mechanical properties. For a better understanding of the mechanical response of biphasic composites, the properties of the individual components are important. Here, the mechanical response

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of flux-grown β-TCP single crystals was investigated for the first time using micro- and nanoindentation techniques.

2. Materials and methods

TCP powder was synthesized by heating a mixture of $Ca_2P_2O_7$ and $CaCO_3$ at 1623 K for 3.5 h. Prior to the heating, the mixture was ball milled for 2 h to achieve a uniformity of composition. The as-synthesized TCP powder was used as a precursor to grow bigger TCP single crystals by flux growth using K_2SO_4 as flux [31]. Typical flux growth involved mixing the TCP powder with K_2SO_4 in the ratio of 1:6 and heat treating in an alumina crucible at 1473 K for 3.5 h followed by furnace cooling. By controlling the flux growth conditions, it is possible to change the size of the crystals (typically 50–75 μm). Finally, these flux-grown TCP crystals were repeatedly washed with hot water to remove the flux and characterized using X-ray diffraction (XRD), scanning electron microscope (SEM) and atomic force microscope to reveal the structural and morphological details of the crystals. Electron backscattered diffraction (EBSD) was performed using a field-emission SEM (FEI, Sirion) to determine the crystallographic orientation of the facets. The Orientation Imaging Microscopy $(OIM)^{TSL}$ software was used to analyze the obtained Kikuchi patterns. Point analysis in EBSD was used to character-

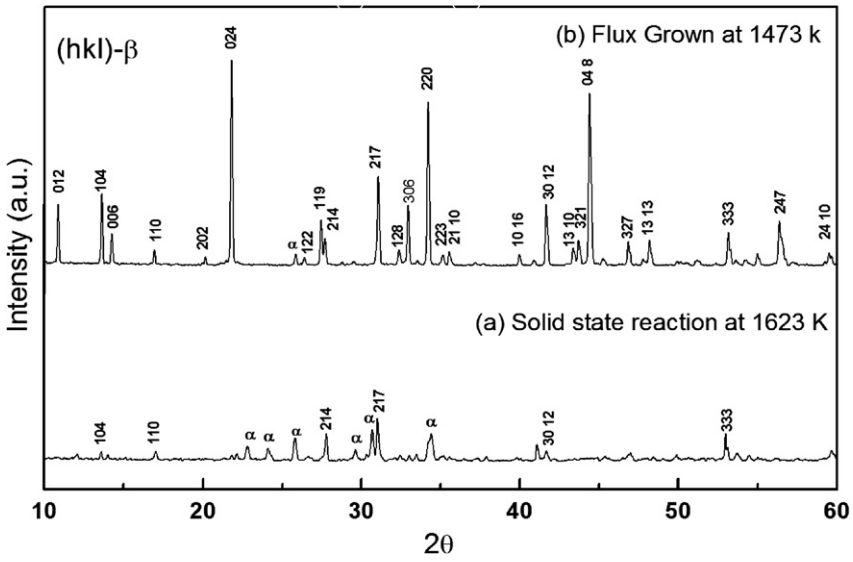

Fig. 1. XRD of (a) TCP powders synthesized by solid-state reaction at 1623 K and (b) β-TCP single crystals grown at 1473 K by flux growth.

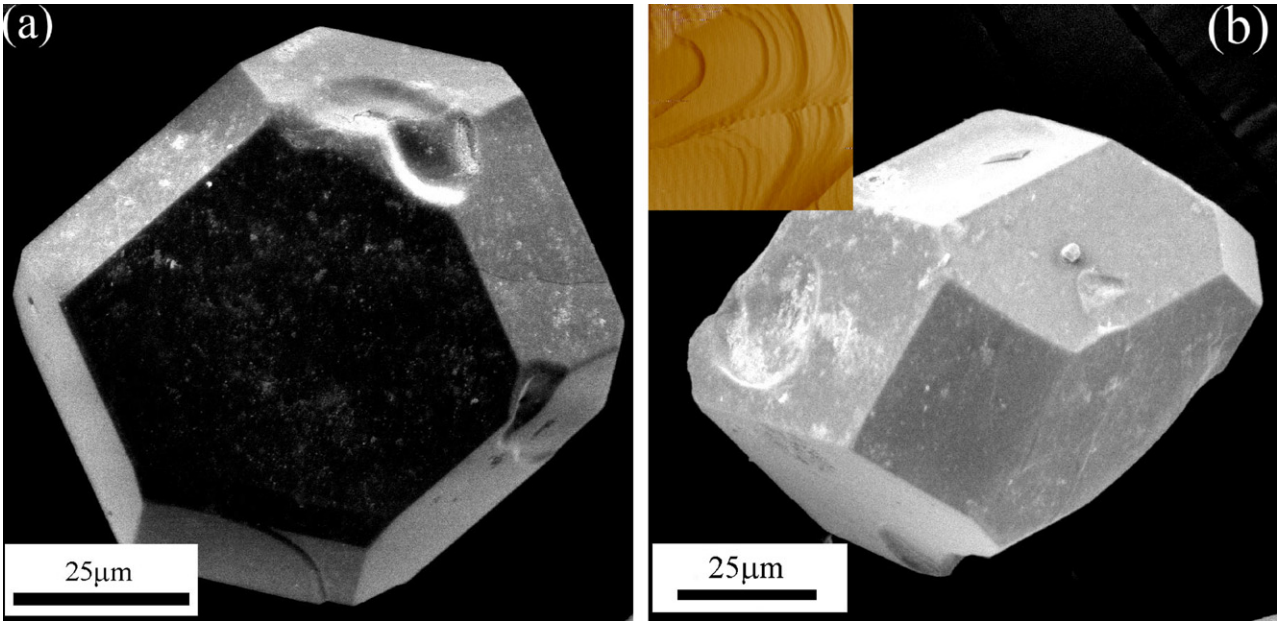

Fig. 2. (a, b) SEM micrographs showing the morphology of the flux-grown β-TCP single crystals at 1473 K. Inset shows the surface steps of the growing facet observed by SPM.