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Variability in the nanoscale deformation of hydroxyapatite during compressive loading in bovine bone

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ABSTRACT

High-energy synchrotron X-ray diffraction is used to study in situ elastic strains in hydroxyapatite (HAP) for bovine femur cortical bone subjected to uniaxial compressive loading. Load–unload tests at room temperature (27 °C) and body temperature (37 °C) show that the load transfer to the stiff nanosized HAP platelets from the surrounding compliant protein matrix does not vary significantly ($p < 0.05$) with temperature. This emphasizes that the stiffness of bone is controlled by the stiffness of the HAP phase, which remains unaffected by this change in temperature. Both the extent of hysteresis and the residual value of internal strains developed in HAP during load–unload cycling from 0 to −100 MPa increase significantly ($p < 0.05$) with the number of loading cycles, indicative of strain energy dissipation and accumulation of permanent deformation. Monotonic loading tests, conducted at body temperature to determine the spatial variation of properties within the femur, illustrate that the HAP phase carries lower strain (and thus stresses) at the anterio-medial aspect of the femur than at the anterio-lateral aspect. This is correlated to higher HAP volume fractions in the former location ($p < 0.05$). The Young's modulus of the bone is also found to correlate with the HAP volume fraction and porosity ($p < 0.05$). Finally, samples with a primarily plexiform microstructure are found to be stiffer than those with a primarily Haversian microstructure ($p < 0.05$).

1. Introduction

Bone is composed of an organic phase (mainly type-I collagen), a mineral phase (calcium hydroxyapatite, $Ca_6(PO_4)_3(OH)_2$ or HAP) and water. These basic components are organized and assembled to form the different hierarchal levels of bone [1]. The HAP phase in bone is usually non-stoichiometric with 4–6% (by weight) carbonate ions substituting for phosphate ions [2,3]. At the macroscopic level, bone is of two types: cortical bone (examined in the present study), which is the dense outer layer of whole bone, and trabecular bone, which is the inner porous region of whole bone. At the microscopic level, cortical bone made up of a number of cylindrical motifs called osteons, each of which contains a central Haversian canal running through its entire length, and aligned with the longitudinal direction of bone. The osteons are made up of concentric sheets of lamellae, which are made up of collagen fibril bundles arranged in various configurations, depending on the structural and functional requirements of the species [1,4]. Water is located at multiple hierarchical levels—in the triple helical collagen molecules, in the collagen fibril and in fibril gaps—mediating mineral–organic interactions [1,5–7]. At the nanoscopic level, bone is modeled as a composite, with HAP, collagen and water as the main constituent phases. HAP is observed as platelets with approximate size $50 \times 25 \times 4$ nm, as determined by X-ray diffraction (XRD) [8,9]. A number of composite models have been proposed to describe the interaction of these two phases and to study their contribution to the bulk behavior of bone. One widely accepted model, which is also used in the present work, suggests that HAP platelets are present as nanoreinforcements distributed throughout a matrix of collagen and water [10–13]. Another model reported recently suggests that HAP and collagen are present as continuous phases and form an interpenetrating composite [3,14,15]. This structure, if confirmed, would necessitate a different model, which is beyond the scope of the paper.

Most mechanical tests conducted so far on bone have focused on the macroscopic-level properties [16–20]. To shed light on the role of the individual phases in the deformation of bones, stresses in the HAP and collagen phases at the lowest level of the structural hierarchy of bone must be measured. Scattering using high-energy, high-intensity X-rays from synchrotron sources provides elastic strain information from phases with sizes as small as few nanometers, averaged over volumes as large as a few cubic millimeters (using a large, unfocused X-ray beam) or as small as a few cubic micrometers (using a focused beam) [21]. This method has been used extensively to study load transfer between matrix and

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