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## Depth-resolved and fatigue studies of thermal sprayed hydroxyapatite coatings

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Hydroxyapatite coatings (HAp composed of  $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$ ), deposited by air-plasma spray onto cylindrical  $\text{Ti}_6\text{Al}_4\text{V}$  rods were investigated in the as-coated and fatigued conditions. Through-thickness characterisation was carried out using conventional X-ray (near surface in reflection mode) and Synchrotron radiation (depth dependence in transmission mode) diffraction of the phase composition, percentage crystallinity, and residual stress. Fatigue investigations were performed on samples submerged in simulated body fluid maintained temperature around  $37^\circ\text{C}$ . Samples were mechanically loaded to  $150, 500$  and  $750 \times 10^3$  tension-compression cycles.

In the as-coated condition, HAp and its thermal decomposition products, tetracalcium phosphate (TTCP), tricalcium phosphate (TCP) and calcium oxide exist throughout the coating thickness. Chemical phase quantification with Rietveld refinement indicates HAp and TTCP to be the major phases. The HAp content is maximum at the coating mid-thickness from where it systematically reduces with depth. The decrease in HAp composition is compensated by an increase in the TTCP content. The coating is most crystalline at the near-surface region, from where it decreases as the coating-substrate interface is approached.

With fatigue treatment, the HAp phase content increases with number of cycles, whereas the TTCP phase content decreases. Residual stress results indicate that the principal components 11 and 33 are respectively tensile and compressive at the surface; both components relax with depth. With further depth a change in stress state at the midpoint for both components is observed.

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