Twinning induced enhancement of fracture toughness in ultra-fine grained Hydroxyapatite-Calcium Titante composites

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Statement of Purpose: Even though Hydroxyapatite (HA) is highly bioactive and biocompatible, some of its properties like very low conductivity and fracture toughness limit its application as a bone replacement material. To address these issues, $CaTiO_3$, which has comparatively good conductivity, has been used as an additive to obtain HA-CT composites with better conductivity and mechanical properties. *In vitro* (Thrivikraman G, Biomaterials 2013;34:7073.) and *in vivo* (Mallik PK, J. Biomed.Mater.Res-A 2014;102:842) studies have already shown that HA-CT composites are excellent for bone regeneration applications. The current study provides a structure - property correlation for the observed enhanced long crack fracture toughness using extensive TEM and EBSD characterization of twins in CT. In addition to this, crack tilt and twist models from fracture mechanics have been used to correlate twin width/ twin density to the enhancement of fracture toughness. The favorable fracture toughness along with moderate conductivity reported in our earlier work make HA-CT composites suitable for bone tissue engineering applications over and above other competing HA based biomaterials.

Methods: Hydroxyapatite powders were synthesized by adopting wet precipitation route. The crystalline calcium titanate ($CaTiO_3$) was synthesized using the mechano-chemical activation of the mixture of CaO and TiO_2 (anatase), followed by calcination at 900°C for 2 hrs. HA-CT powder mix with varying amounts of CT (40, 80 wt. %) were obtained by ball milling (Fritsch, Pulverisette 1583, Germany) for 16 hrs using agate balls and jars as grinding media with ball to powder ratio of (1:4). The multistage spark plasma sintering technique (MSSPS) (Dr. Sinter, Model 515S, SPS syntax Inc, Japan) was used to sinter the powders. The fracture toughness of HA-CT composites was determined by three point bending test (Instron 1195, Buckinghamshire, England) using single edge V-notched beam (SEVNB) technique. Scanning Electron Microscope (SEM, FEI quanta 200) equipped with Electron Backscatter Diffraction (EBSD) was used to carry out orientation analysis with commercial Orientation Imaging Microscopy software (TSL-OIM). The samples for EBSD analysis were prepared by polishing with SiC papers and diamond paste and colloidal silica (Struers OPS). The polished samples were etched at room temperature by anhydrous citric acid and DI water in the ratio of 8:10 (by mass) and adding 2-3 drops of hydrofluoric acid (HF) for about 5 min. The finer microstructural features of the CT and HA-CT composites were investigated by Transmission Electron Microscope (TEM, Tecnai G^2). For TEM imaging, electron transparent thin samples of thickness 100 nm were prepared using ultrasonic disc cutter, followed by dimpling and precision ion polishing system (PIPS, Gatan 691).

Results: The fracture toughness was found to be highest (1.7 MPa $m^{1/2}$) for HA-40%CT composites, which is almost twice that of pure HA and highest among the HA based ceramic composites (Fig.1). In the present case, the experimentally measured twin width (λ) from TEM images was found to increase non-linearly with grain size (d) in in CT grains of sizes less than 10 μm and their relationship agrees well with the theoretical prediction ($\lambda \propto d$). Analysis using TEM Bright Field (BF) and Dark Field (DF) along with Selected Area Electron Diffraction (SAED) revealed the presence of undissociated HA and CT, with twins in CT grains. From SAED along [100] zone axis, the twins were identified to be due to 180° rotation around [101]. The twins were further characterized by EBSD to obtain Kikuchi patterns and twin orientation relationship was determined in the form of a misorientation matrix along with misorientation angle (92°).

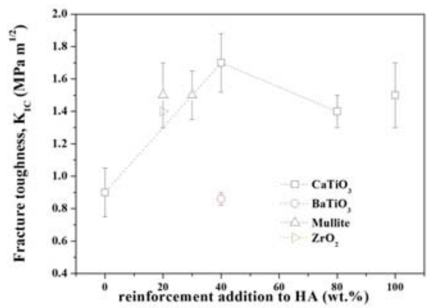

Fig.1: Comparison of K_{Ic} values of HA based composites

Conclusions: The addition of $CaTiO_3$ to HA substantially increases the strength and long crack fracture toughness properties compared to pure HA. The measured fracture toughness is the highest among HA based ceramic composites and closer to the fracture toughness of cortical bone (2-12 $MPa^{1/2}$). The microstructure of HA-$CaTiO_3$ composites reveals twinned $CaTiO_3$ grains of sizes around 1-2 μm. TEM analysis shows that the observed twinning is due to the 180° rotation around the [101] direction in orthorhombic CT. The twin density and twin width/ interlamellar spacing are found to decrease with an increase in $CaTiO_3$ content, also, it is seen that the equilibrium twin width for HA-CT composites match reasonably well with the observed values. EBSD of CT enabled us to establish the twin crystallographic relationship in the form of misorientation angle: 92°. These high angle boundaries are expected to contribute positively towards the fracture toughness enhancement of the composite.