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Inhibited grain growth in hydroxyapatite–graphene nanocomposites during high temperature treatment and their enhanced mechanical properties

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ABSTRACT

Nanostructured hydroxyapatite (HA)–graphene nanosheet (GN) composites have been fabricated by spark plasma sintering consolidation. Nanostructural evolution of the bioceramic-based composites during further high temperature heat treatment is characterized and enhanced mechanical strength is assessed. GN keeps intact after the treatment and its presence at HA grain boundaries effectively inhibits HA grain growth by impeding interconnection of individual HA grains. Microstructural characterization discloses strong coherent interfaces between GN and the (300) plane of HA crystals. This particular matching state in the composites agrees well with the competitive theoretical pull-out energy for single graphene sheet being departed from HA matrix. The toughening regimes that operate in HA–GN composites at high temperatures give clear insight into potential applications of GN for ceramic matrix composites.

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1. Introduction

As one of the most popular bioceramics, hydroxyapatite (HA) has been extensively employed for biomedical applications. Yet, regardless of the successful application of HA in orthopedic surgery for promoting fast fixation of bony tissues, there are still concerns related to its long-term performances, i.e., intrinsic brittleness and low fracture toughness of HA. Tremendous efforts have therefore been made in past decades towards improving its strength and toughness by adding a second phase for load-bearing applications [1–5]. In general, composite materials have a structure comprising two or more components that differ in physical and chemical properties which have been combined to provide specific characteristics for particular applications. Enhancing stiffness and strength and precise property matching are always the predominant concerns in design and processing of the ceramic matrix composites. The discovery of graphene and its derivatives has sparked considerable interests in their use as reinforcements in various matrix materials to impart stiffness, strength, and toughness [6,7]. The 2D nature of graphene also confers on itself appropriateness of high pressure processing. Graphene could

therefore be applied as an excellent reinforcement to ceramic materials. Recent studies on graphene-nanoplate reinforced composites like poly lactic acid [8], ultra-high-molecular-weight polyethylene [9], silicon nitride [10] and aluminum [11] already shed light on enhanced mechanical or biological properties. Incorporation of graphene nanosheet (GN) into HA could be a promising option for enhancing the biological properties of HA for biomedical applications and significantly enhanced strength has been previously revealed for HA–GN composites [12]. Biomedical application has been one of the exciting opportunities of graphene that inspired extensive explorations [13,14]. Of particular interests are graphene-based nanomaterials and their exciting biological performances [15,16]. In the light of available scientific evidences suggesting its biological performances, graphene might potentially be a good candidate for HA-based composites for biomedical applications. Compared to the conventional ceramic matrix composites reinforced by one-dimensional carbon materials such as carbon fibers, carbon nanotubes or ceramic whiskers [17–19], the further significantly enhanced fracture property of graphene-containing composites reported in recent years was ascribed to strong interfacial bonding as a result of mechanical interlocking between graphene and the matrix due to the nanoscale roughness of the platelets [6,20]. Our results have shown that the predominant toughening mechanisms for HA–GN nanocomposites are fine grain strengthening, graphene flakes pull-out, microcrack

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toughening, crack deflection at the HA–GN interface and crack bridging by GN [12].

It is known that high temperature heat treatment is usual for HA-based bioceramics [21]. The treatment offers the benefits of tuning phases [22], modifying topographical structures [23], and enhancing mechanical strength [24] or bioactivity [25] of the biomaterials. However, for GN-containing composites, post heat treatment might raise the problems of grain growth, decomposition, deteriorated residual stress and cracking, or structural changes of graphene at elevated temperatures [26]. To the best knowledge of the authors, behaviors of ceramic–GN composites in bulk form after heat treatment are not established yet, which would hinder potential extensive applications of GN. In this study, bulk HA–GN composites consolidated by spark plasma sintering (SPS) were heat treated for enhanced mechanical strength. Thermally induced structural damage to graphene platelets has not been seen. Direct evidence has shown that the unique presence of GN at HA grain boundaries critically inhibit HA grain growth, giving rise to promoted toughening in the composites. GN–HA interfacial adhesion and toughening mechanisms for the GN-containing composites after the heat treatment were also comprehensively elucidated.

2. Materials and methods

HA–GN nanocomposites pellets with the thickness of 5 mm have been consolidated by SPS, detailed procedure of which has been reported in detail previously [12]. To enhance the performances of the composites, post heat-treatment was performed at 800 °C with the keeping time of 2 h in a vacuum (2×10^{-2} Pa) sintering furnace (ZQL-80, China). Microstructure examination of the samples was conducted using transmission electron microscopy (TEM, FEI Tecnai F20, the Netherlands) and field emission scanning electron microscopy (FESEM, FEI Quanta FEG250, the Netherlands). Fracture properties of the pellets were measured by indentation testing made on their polished surfaces under a load of 300 gf with the loading time of 10 s using HV-1000 (Shanghai Lianer Testing Equipment Co., China). Fracture toughness (K_{IC}) of the pellets was derived from the indentation approach according to the Anstis equation [27]: $K_{IC} = 0.016(E/H)^{1/2}(P/C^{3/2})$, where H is the measured hardness, P is the applied load, E is elastic modulus, and C is length of the crack initiated by the indentation under the load of 1000 gf. Average microhardness value for each specimen was acquired from 10 indents. Elastic modulus of the samples was determined by nanoindentation test carried out using a standard Berkovich indenter on nanomechanical test system (NANO G200, MTS, USA). The maximum indentation depth chosen for the present test was 1 μ m. At least 10 indentations were made for an average value for each sample.

The experimental configuration for assessing fragmentation properties of solids has been reported by other researchers [28]. In this work, impact resistance and dynamic failure mechanism of the HA and the HA–GN composites was examined. Briefly, the SPS HA and HA–GN samples were prepared in the form of solid disks and launched with an impactor–plate facility to the impact velocity of 5.48 m/s. The diameter of the launch tube used was 10 mm. Stainless steel spheres of 9.06 ± 0.02 mm in diameter were used. The measured mass was 2.96 ± 0.02 g. Fracture surfaces of the specimens were characterized using a laser confocal microscope (ZEISS, LSM700, Germany). Both three-dimensional computer-based topographic maps and roughness parameters were acquired from the measurements.

3. Results and discussion

After the SPS consolidation, even dispersion of GN in the composites has been revealed and GN can be clearly seen at HA grain boundaries (Fig. 1). It is noted that, based on the TEM characterization, the GN-containing HA compacts show finer HA grains and the increase in content of GN gives rise to further refined HA grains (Fig. 1c-1 versus b-1). Mean HA grain size in the HA–0.1 wt% GN and the HA–1.0 wt%GN compact is ~ 250 nm and ~ 150 nm respectively, while the GN-free HA sample shows the grains of ~ 1.5 μ m. It has been realized that during the synthesis of the HA–GN nanocomposite powder, HA grains nucleate on and grow along graphene sheets [12]. SPS is essentially a high temperature processing route, regardless of the short duration offered by the approach. The graphene sheets in the SPS composites obviously inhibit the rod-like nano HA grains from growing along at least one direction, which likely accounts in part for the finer HA grains in the GN-containing SPS samples. This effect is more pronounced in the pellets with higher content of GN.

After the heat treatment at 800 °C for 2 h, it is unsurprising to note that for the pure HA sample, HA grain growth took place with rapid continuous movement of grain boundaries in a uniform manner, showing significantly enlarged grain size of over 2.5 μ m (Fig. 1a-2). In contrast, however, there is less grain growth in the HA–GN samples under the same heat treatment conditions (Fig. 1b-2 and c-2). The mean HA grain size in the HA–0.1 wt%GN and HA–1.0 wt%GN composites is ~ 320 nm and ~ 200 nm respectively, suggesting the predominate role of GN as grain growth inhibitor during the high temperature annealing by pinning grains together and impeding boundary diffusion. The size increase of HA grains is mostly seen for those without intimate contact with GN. The grains located at the places where no GN is detected are much bigger (Fig. 1c-2). In fact, GN existing at HA grain boundaries forms continuous wall zones, in turn isolates HA grains from neighboring ones (Fig. 2a). Consequently, HA grain growth along at least one direction can be effectively restrained, which presumably accounts for the finer HA grain sizes in the GN-containing HA composites. In the HA–GN pellets, grain growth is recognized for the grains growing at a high rate along the path where no GN is present, while the neighboring grains are consumed (Fig. 2a). This results in the typical microstructure of the HA–GN composites with a few very large grains. In order for this phenomenon to occur, the subset of prefer-to-grow grains must possess some advantages over their competitors, for example high grain boundary energy, locally high grain boundary mobility, favorable texture or lower local second-phase density. Even though the mechanism about the above grain growth is not known yet, the GN-restrained irregular grain growth of HA can be schematically depicted (Fig. 2b). SPS processing brought about significant changes of HA grains from rod-like shape to irregular configuration. Even dispersion of GN effectively slows down or freezes the growth of HA grains, which prevails through retarding grain boundary migration. Further high temperature heat treatment results in slight growth of the HA grains staying far away from GN or irregular growth along the direction parallel to GN for the grains intimately contacting GN. GN works favorably as inhibitor preventing remarkable growth of HA grains. It is anticipated that more GN in the HA-based composites would more effectively restrict grain growth of HA during high temperature processing, which usually takes place during fabrication of bulk HA for biomedical applications. This feature should be closely related to grain-size-dependent mechanical properties of the composites.

Assessment of the properties of the heat-treated nanocomposites showed that Young's modulus values increased from 100.4 GPa for the pure HA to 110.3 GPa for the HA–0.1 wt%GN and 148.2 GPa for the HA–1.0 wt%GN pellets. After 2 h treatment at

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