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Boron nitride nanoplatelets induced synergetic strengthening and toughening effects on splats and their boundaries of plasma sprayed hydroxyapatite coatings

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ABSTRACT

Boron nitride nanoplatelets (BNNPs) with excellent mechanical properties were introduced into HA coatings fabricated through plasma spray in this research. SEM observation and Raman results revealed the added BNNPs retained their original structure even after harsh process and distributed homogeneously in the as-sprayed coatings. As compared with the monolithic HA coating, a 2.0 wt%BNNP/HA coating exhibited significant improvement (~ 40.3%) in fracture toughness and moderate enhancement (~ 20.0%) in indentation yield strength. Synergetic strengthening and toughening mechanisms which are operative through splat boundaries and individual splats were proposed. At splat boundaries, these embedded BNNPs induced stronger adhesion between the adjacent splats to resist splat sliding, which is evident from the fact that the calculated inter-splat friction force of an as-sprayed BNNP/HA coating was increased by ~7.3% at 2.0% BNNP weight fraction. Within splats, toughening mechanisms such as BNNP pullout, crack bridging by both anchored BNNPs and nanosized HA grains, crack deflection and crack propagation arrested by the embedded BNNPs were observed to improve toughness. Moreover, thermal mismatch between HA matrix and BNNPs during cooling process after plasma spray would induce the pre-existing dislocations formed around these BNNP nanofillers, which was assumed to hold out the effect of Orowan-type strengthening within splats.

1. Introduction

Metallic implants usually made of titanium alloys (Ti-6Al-4V) are widely clinically used to repair and/or replace these diseased/damaged bones owing to their good mechanical properties (high fracture toughness), low density and relatively high corrosion resistance [1]. However, the poor wear resistance and the inferior adhesion bonding with the bone tissues due to bio-inert in nature are demonstrated to impair their long-term clinic performance. Therefore, biologically compatible coatings deposited on the surface of the metallic implants have been increasingly recognized as extremely attractive and effective way for promoting osteointegration and interfacial bonding with the surrounding bone cells [2]. Among various biocompatible materials, hydroxyapatite (HA), a major inorganic constituent of natural bone exhibits excellent bioactivity/osteointegration properties [2,3], has been extensively investigated for biomedical applications. Nevertheless, the inferior fracture toughness limits its wide applications as a coating material, especially on the load-bearing metallic implants, and therefore toughening HA coating has been one of the most concerned topics in the materials community [4]. To this end, second phases such as alumina (Al_2O_3) [5,6], yttria-stabilized zirconia (YSZ) [7,8], titania [9,10] have been introduced to enhance fracture toughness of the HA coatings. Despite significant improvement achieved in fracture toughness of these HA composite coatings, it should be noted that the addition contents of these ceramic particles, basically biologically inert, are usually as high as 30–50% weight fraction, inevitably leading to degradation of the excellent bioactivity associated with HA. Hence, an ideal reinforcement in HA composites and/or coatings should possess significant toughening effect even with smaller amount addition to avoid negative influence on the bioactivity/osteointegration of HA.

In recent years, carbonaceous nanomaterials such as carbon nanotubes (CNTs) and graphene have been considered as promising nanofillers in ceramics to improve their fracture toughness [11,12] due to their excellent mechanical properties, which open new material-design avenue to HA composites/coatings. For example, the fracture toughness showed a ~56% improvement with a CNT addition of 4.0 wt% (weight percentage) in a plasma-sprayed HA composite coating [13,14]. Nevertheless, the available results on the biocompatibility of CNTs are inconsistent, though some studies ascribed the cytotoxicity of CNTs to the presence of metallic catalyst particles rather than CNT itself [15].

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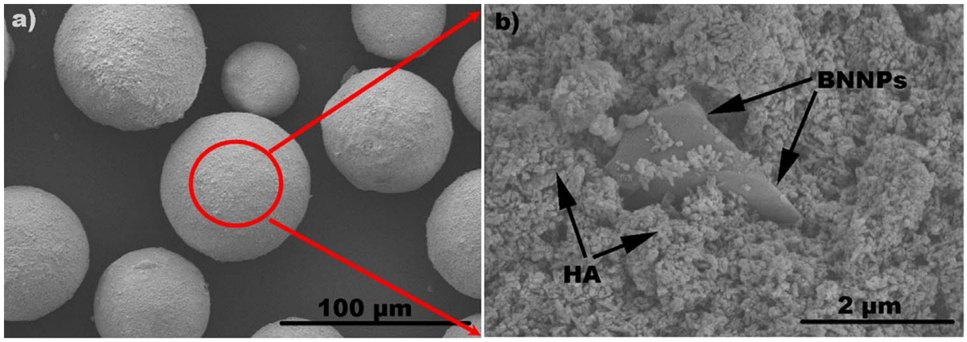

Fig. 1. SEM images showing (a) spray-dried agglomerated BNNP/HA composite powders and (b) distribution of BNNPs on the surface of a spray-dried nanostructured agglomerate.

Unlike CNTs, graphene can be synthesized in such pure ways as chemical vapor deposition, micromechanical exfoliation of graphite [16]. Our previous preliminary study has demonstrated that graphene nanosheet (GNS) reinforced HA composite displayed ~80% improvement in fracture toughness at 1.0 wt% GNS concentration [17]. However, it is noteworthy to mention that lower oxidation temperature (~ 400–450 °C) of carbonaceous nanomaterials [18] makes them not suitable as nanofillers in composites for high-temperature applications or composite synthesized through the high-temperature processes.

Boron nitride nanoplatelets (BNNPs) with two-dimensional structure possess comparable mechanical properties (e.g. tensile strength ~ 35 GPa, elastic modulus 700–900 GPa) [19] to those of carbonaceous nanomaterials. Most importantly, BNNPs are chemically inert up to 950 °C[20], which is advantageous over CNTs and graphene. Very recently, Yue et al. [21] found that the fracture toughness of a ZrB_2-SiC composite increased by up to ~ 24.4% at 1.0 wt% of hybrid mixture of BNNPs and BN nanotubes (BNNTs), and the fracture toughness of a BNNP/Si_3N_4 composite possessed an increase of 23.6% at 1.0 wt% BNNP addition [22]. Furthermore, Lahiti et al. [23] reported that BNNTs are non-cytotoxic to osteoblasts, and their presence in a HA composite does not negatively affect proliferation and viability of osteoblasts, implying that BNNPs might be a promising toughening agent in the HA composites. Additionally, as compared with black color associated with carbonaceous nanomaterials, white color of BNNPs matches well with that of HA. Hence, from the viewpoint of visual impression, BNNPs are more potential in HA matrix for orthopedic applications.

Plasma spray is an industrially versatile surface coating technique owing to the cost efficiency and simplicity of the process [24], and it is also a US Food and Drug Administration (FDA) approved technique for depositing HA coating on implants for clinical applications [15]. It is well known that the as-sprayed coatings usually have lamellar structure due to stacking of thin splats, which are produced by the molten or partially molten droplets impacting on the substrate followed by flattening and rapid solidification. These adjacent splats bond together at different length scales intercepted by voids, inter-splat pores and microcracks, leading to relatively weak bond strength between the adjacent splats. As a result, splat sliding usually occurs, and subsequently degrading the mechanical properties of the as-sprayed coatings [25–27].

In view of the present scenario, the aim of this research was to present a systematic investigation on the mechanical properties of BNNP reinforced HA composite coatings fabricated through plasma spray, and the synergetic strengthening and toughening mechanisms through these splat boundaries and individual splats of the as-sprayed HA composite coatings were highlighted.

2. Material and methods

2.1. Materials and coating fabrication

HA nanorods with a diameter of ~ 20 nm and a length of ~ 100 nm (Nanjing Emperor Nano Material, China) and BNNPs with a thickness of ~ 20–30 nm and a diameter of ~ 0.5–5 µm (Nanjing XianFeng Nano Material Company, China) were employed as precursor materials. To ensure homogeneous distribution of BNNPs in the HA composite coatings, the as-received BNNPs were ultrasonicated for 3 h in ethanol with a concentration of about 0.1 mg/ml. Then, HA nanorods were added into BNNP suspension followed by 1 h ultrasonication and 3 h magnetic stirring, respectively. Finally, the obtained composite powders were dried in an oven at 80 °C for 24 h. The compositions chosen here were pure HA, 1.0 wt%BNNP/HA and 2.0 wt%BNNP/HA.

The nanosized powders cannot be directly thermally sprayed using the regular powder feeders due to the fact that these tiny particles usually clog the hoses and fittings used for powder transportation. Also, very lower inertia along with the individual nanoparticles cannot penetrate the stagnation layer at the substrate, leading to low deposition efficiency. Herein, spray drying was employed to obtain microsized agglomerates with good flowability for plasma spray. These HA nanorods and BNNP-HA composite powders were dispersed in a water-soluble organic binder (Polyvinyl Alcohol), the suspension was sprayed in an atomized chamber of a spray drier (LGZ-8, Wuxi Dongsheng Spray-Granulating and Drying Equipment Plant, China), and then dried to obtain porous spherical nanostructured agglomerates with a diameter of 40–75 µm (Fig. 1a). Moreover, it is evident from Fig. 1b that BNNPs distributed homogeneously on the surface of a spray-dried agglomerated composite powder.

Prior to plasma spray, Ti-6Al-4V substrates (100 mm × 15 mm × 5 mm) were blasted using Al_2O_3 particles with an average size of ~1 mm and followed by being cleaned with acetone. These spherical spray-dried agglomerates were plasma sprayed using SG 100 gun (Praxair Surface Technology, Danbury, CT) on Ti-6Al-4V substrates, in which 20–25 kW plasma power and 600–700 A plasma-gun current were used with a powder feeding rate of 4.5 g/min and a standoff distance of 100 mm. Argon was used as the primary gas (flow rate: 32 slpm) with helium as an auxiliary gas (28 slpm). Argon was also used as powder carrier gas (8 slpm).

2.2. Microstructure and mechanical characterizations

The cross-section of the as-sprayed HA and BNNP/HA coatings was metallographically polished for microstructure characterization and instrumented microindentation. X-ray diffraction (XRD, X′Pert-ProMRD, Holland) with Cu K_α radiation was conducted to analyze the phase constituents of the as-sprayed coatings using a scanning rate of 5°/min. Micro-Raman spectroscopy (Renishaw, UK) with an Argon ion laser of wavelength 633 nm and an acquisition time of 10 s was employed to confirm the existence of BNNPs in the as-sprayed coatings.