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Impedance spectroscopy and mechanical response of porous nanophase hydroxyapatite–barium titanate composite

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ABSTRACT

The present study aims to develop the porous nanophase hydroxyapatite (HA)–barium titanate (BT) composite with reasonable mechanical and electrical properties as an electrically-active prosthetic orthopedic implant alternate. The porous samples (densification ~40–70%) with varying amounts of BT (0, 25, 35 and 100 vol.%) in HA were synthesized using optimal spark plasma sintering conditions, which revealed the thermochemical stability between both the phases. The reasonably good combination of functional properties such as compressive [(236.00 ± 44.90) MPa] and flexural [(56.18 ± 5.82) MPa] strengths, AC conductivity [7.62×10^{-9} (ohm-cm)$^{-1}$ at 10 kHz] and relative permittivity [15.20 at 10 kHz] have been achieved with nanostructured HA-25 vol.% BT composite as far as significant sample porosity (~30%) is concerned. Detailed impedance spectroscopic analysis was performed to reveal the electrical microstructure of developed porous samples. The resistance and capacitance values (at 500 °C) of grain (R_G, C_G) and grain boundary (R_{GB}, C_{GB}) for the porous HA-25 vol.% BT composite are (1.3×10^7 ohm, 3.1×10^{-11} F) and (1.6×10^7 ohm, 5.9×10^{-10} F), respectively. Almost similar value of activation energy (~1–1.5 eV) for grain and grain boundary has been observed for all the samples. The mechanism of conduction is found to be same for porous monolithic HA as well as composite samples. Relaxation spectroscopic analyses suggest that both the localized as well as long range charge carrier translocations are responsible for conduction in these samples. The degree of polarization of porous samples has been assessed by measuring thermally stimulated depolarization current of the poled samples. The depolarization current is observed to depend on the heating rate. The maximum current density, measured for HA-25 vol.% BT sample at a heating rate of 1 °C/min is 2.7 nA/cm^2. Formation of oxygen vacancies due to the reduced atmosphere sintering contribute to the space charge polarization, which is obtained as the dominant polarization mechanism in the developed porous samples. Overall, such integrated functional responses do establish spark plasma sintered porous HA–$BaTiO_3$ nanocomposite as potential alternative for electroactive prosthetic orthopedic implants.

1. Introduction

Owing to the fact that the externally applied electrical stimulation can potentially enhance the osseointegration *in vitro* and *in vivo*, a significant attention has been drawn towards understanding the dielectric and electrical properties of the developed orthopedic implant materials [1–8]. The natural bone is an electrically-active porous nanocomposite material with the porosities of the cortical and cancellous bones are 10–30% and 30–90%, respectively [9–11]. The inherent electrical activities of bone assist in its development, maintenance as well as fracture healing [9,12,13]. A composite of bioactive hydroxyaptite (HA) with the perovskite $BaTiO_3$ (BT) has been demonstrated as a potential alternative for electro-active orthopedic implants in a number of *in vitro* as well as *in vivo* studies [14–16]. The inclusion of ferroelectric BT as secondary phase in HA has been suggested to significantly improve the dielectric and electrical behavior as well as fracture toughness of HA [17,18]. BT converts the applied mechanical energy into electrical energy by virtue of its piezoelectricity. Platt et al. [19] suggested that the encapsulation of piezoelectric ceramics with the orthopedic implants can assist in monitoring the performance of implant by producing *in vivo* electrical energy in response to external mechanical stimuli. Such technique has been suggested to be useful to diagnose any kind of abnormality in the vicinity of implant at very early stages.

The nanostructured ceramics possess wide spectra of improved functional (electrical and mechanical) response as compared to the conventional ceramics [20]. In addition, the nanophasic biomaterial platform can improve the osteogenic ability. The nano-sized grains stimulate adhesion of bone cells in contrast to the micron-sized grains of same material [21]. The improved biological response of nanophase bioceramics for osteoblast cells has been demonstrated *in vitro* as well as *in vivo* [22].

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The chemistry as well as topography at the implant-host interface decides the initial success of implant [23]. The porosity is one of the important topographical factors in bone graft applications for the effective bridging, which provides mechanical interlocking at the graft-host interface [24]. Porous HA promotes osteogenesis as compared to its dense counterpart [25]. Nanoporosity can further enhance the bioactivity [26]. Nanostructure can modify the cellular response as compared to the conventional surfaces [27]. However, the porosity degrades the electrical and mechanical response significantly. Spark plasma sintering (SPS) has been suggested as one of the promising approaches in developing the porous ceramic scaffolds with reasonable mechanical strength as well as nanostructured ceramics [28–31]. It has been reported that the spark plasma sintering of ferroelectric BT led to the formation of nano-sized domains, irrespective of initial particle size, which increases its polarizability [32].

The electrically polarized surfaces of HA have been demonstrated to accelerate the osteoblastic activity and consequently, the new bone formation [5–7,33]. One of the possible ways to increase the polarizability of ferroelectrics, such as BT- based composite system is to retain the fine grain size in the sintered microstructure. The nanosized grains increase the polarizability of BT phase as compared to the micron sized grains [34]. Because of the higher fraction of grain boundaries in the nanostructured ceramics than conventional structure, the polarizability of nano-grain ceramics can be enhanced significantly. Owing to the high surface area of porous samples, the polarization can be increased considerably as compared to dense samples [35]. It has been demonstrated that the polarization of porous hydroxyapatite-based bioceramic facilitates faster osteointegration with the host tissue [36].

Therefore, the development of the porous nanophase bioceramics has attracted attention to achieve the desirable combination of electrical and mechanical properties prior to the realization of the clinical implications. The integration of above consequences suggests that the porous nanophase HA-BT composite can actively promote the osseointegration. To this perspective, the present study attempted to develop a porous nanophase HA-BT composite with varying amount of BT in HA using the spark plasma sintering technique. The processing parameter was optimized to avoid the evolution of other phases due to reaction between HA and BT phases or the dissociation of HA phase. Further, the mechanical and detailed impedance spectroscopic analyses were performed for optimal composite in reference to its constituent phases.

2. Experimental

2.1. Material processing

Commercially available HA (<200 nm, Sigma Aldrich, USA) and BT nanoparticles (Wako, Japan) were used in the present study. The particle size of BT (d_{50} ~150 nm) was analyzed with the nano particle size analyzer (SALD-7100, Shimadzu, Japan) using ultraviolet laser. The HA-xBT composites were prepared by ball milling the varying amount of BT (x = 0, 25, 35, 100 vol.%) with HA for 6 h in acetone using polyethylene jar and zirconia balls. The slurry was dried using rotary vacuum evaporator (Eyela, N-1100). The HA, BT and their composite nanopowders were weighted for 1.5 mm thick sample in 10 mm diameter graphite die. The height of the graphite punches was adjusted using 1 mm thick graphite spacers to avoid the application of pressure during sintering. In order to obtain the range of porosity values in the sintered samples, the nanopowders were pre-pressed uniaxially at 0 (P1), 10 (P2), 20 (P3) and 30 MPa (P4), respectively and then the pressureless spark plasma sintering was performed to consolidate the porous powder assembly. The optimal processing parameter for these samples, without any reaction between the constituent phases, was obtained to be 850 °C for 30 min (not shown). The samples were heated at 50 °C/min and cooled following the furnace cooling. Prior to reaching the sintering temperature of 850 °C, the powder assembly was kept at 650 °C for 5 min for initial surface activation. The sintered samples were annealed at 700 °C for 2 h in air to remove the carbon contamination. It has been reported that the sintering of HA above 850 °C in vacuum leads to the dehydration of hydroxyl ions from the HA lattice [37].

2.2. Densification, phase evaluation and morphological assessment

The bulk densities of porous samples were calculated using mass and geometrical volume of the sintered compacts. X-ray diffraction (XRD, Philips X' pert, Cu-Kα) analysis was performed to examine the presence of phases in the sintered samples. To confirm the functional groups, Fourier transform infra-red spectroscopic analysis (FT-IR, FT/IR-6300, JASCO) was carried out in the range of 4000–400 cm^{-1} in vacuum. Scanning electron microscopy (SEM, Jeol JSM-7001F) was used to observe the microstructure of the fractured sample surfaces.

2.3. Compressive and flexural strengths

The compressive strength was measured using the cylindrical samples of diameter and thickness of 2 and (2–2.5) mm, respectively. The samples were fractured under compressive load of 2 kN and crosshead speed of 0.05 mm/min using Shimadzu EZ-LX instrument. The flexural strength of rectangular samples with dimensions of $(10 \times 2 \times 2)$ mm^3 was measured using 3 point bend test method. The samples were fractured with load and crosshead speed of 500 N and 0.1 mm/min, respectively using Instron 5582 instrument.

2.4. Impedance spectroscopic analysis

For the impedance measurement, the polished samples were electroded using double electroding method to reduce the dielectric losses as well as to realize the equipotential surfaces. Initially, the porous samples were gold coated, which was then followed by electroding with Ag-Pd paste. The Ag-Pd paste was cured at 700 °C for 5 min. To reveal the electrical microstructure of the developed porous samples, impedance spectroscopic analysis was performed using LCR meter (NF ZM2355) in the temperature and frequency ranges of 25–500 °C and 0.1 Hz–55 kHz, respectively. The data were collected during the cooling cycle. A wide range spectra of dielectric constant [$\varepsilon_r = -Z^{//}.t/(Z^{/2} + Z^{//2}).\varepsilon_0 \omega A$; where, $Z^{/}$ and $Z^{//}$ represent the real and imaginary components of complex impedance, ε_0 is the permittivity of free space and $\omega(=2\pi f)$, t and A are angular frequency, thickness and area of the sample, respectively], AC conductivity [$\sigma_{ac} = Z^{/}.t/(Z^{/2} + Z^{//2})A$] and phase angle [$\theta = \tan^{-1}(Z^{//}/Z^{/})$] were also studied in the similar range of frequency and temperature [4].

It has been suggested that the consideration of constant phase element (pseudo capacitance) instead of pure capacitance is more appropriate in the cases where the center of the semicircular arc lies below the real X-axis [38]. The electrical transport properties of grain and grain boundaries and corresponding activation energy values are also evaluated.

2.5. Thermally stimulated depolarization current (TSDC) measurement

The polarizability of the developed porous samples was examined by measuring the thermally stimulated depolarization current (TSDC). The samples were polarized in silicon oil at temperature and electric field of 150 °C and 3 kV/mm, respectively, for 1 h. The samples were then cooled down to room temperature under the continuous exposure of polarizing field. The poled samples were kept for 1 day to disappear the space charges before measuring the depolarization current. The degree of polarization was measured using picoammeter (Keithley 6487), while heating the poled samples up to the temperature of 500 °C at various heating rates of 1, 3, 5 and 10 °C/min, respectively.