Phase analysis, mechanical properties and in vitro bioactivity of graphene nanoplatelet-reinforced silicon nitride-calcium phosphate composites

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ABSTRACT

The aim of this study is to produce highly dense Si₃N₄ based composites with good mechanical properties and bioactivity. Si₃N₄ ceramics without using sintering aids, Si₃N₄-HA and Si₃N₄-HA-GNP based composites have been produced by spark plasma sintering (SPS) at temperatures of 1525–1550°C. The effect of reinforcement type and content on the densification behavior, phase analysis, microstructural development, mechanical properties, and in-vitro bioactivity behavior of Si₃N₄ were systematically investigated. Monolithic Si₃N₄ that contains a high amount of β-Si₃N₄ phase (~87 wt%) was produced by nearly full densification (~99%). Hydroxyapatite (HA) was used as a starting powder during the preparation of binary and triple composites to provide bioactivity to Si₃N₄, and after sintering, HA transformed into tricalcium phosphate (β-TCP and α-TCP) polymorphs. The incorporation of GNPs had a positive effect on the stability of β-TCP phases at higher sintering temperatures. The improvement in indentation fracture toughness of the samples with GNP reinforcement was mainly attributable to pull-out and crack deflection mechanisms. In-vitro bioactivity of GNP added composites enhanced with increasing α-TCP content. More calcium phosphate-based particle formation was observed in Si₃N₄-HA-GNP composites compared to the Si₃N₄-HA.

1. Introduction

Silicon nitride (Si₃N₄) ceramics have been extensively studied for more than 60 years [1]. Si₃N₄ is a structural ceramic, exhibits a low density, high hardness, excellent thermal shock resistance, high-temperature strength, excellent wear resistance, high chemical inertness, and high fracture toughness. These properties make them a candidate material for aerospace and automotive engine components, high-temperature gas turbines, glow plugs, bearings for industrial applications, welding and burner nozzles, and mineral processing [2]. Moreover, Si₃N₄ ceramics are biocompatible, anti-microbial [3] and radio transparent, which enable them visible under X-ray, magnetic resonance imaging (MRI), and computerized tomography (CT) [4,5]. The combination of these properties gives Si₃N₄ the potential to be used as a bioceramic for high load-bearing components of the prosthetic knee and hip joints.

Si₃N₄ is currently used as cervical spacers, and spinal fusion implants, and has been implanted in human patients for over 10 years [5]. Si₃N₄ as a biomaterial has some advantages in comparison to metallic biomaterials such as titanium (Ti) and cobalt-chromium (Co-Cr) alloys, oxide bioceramics such as alumina (Al₂O₃), and biopolymers such as polyether ether ketone (PEEK), and high-density polyethylene (HDPE). For instance, Si₃N₄ has higher fracture toughness and ability to withstand rapid temperature changes than that of Al₂O₃ [1,4], and better wear resistance than HDPE. The partial radiolucency is an advantage of Si₃N₄ for being visible on plain radiography when used as a plate or screw in maxillofacial surgery. Since metals are radio-opaque, the underlying tissue cannot be visualized [5].

Moreover, studies showed that Si₃N₄ exhibits non-cytotoxicity, high antibacterial function, greater new bone formation and better osseointegration in comparison to Ti and PEEK [6]. Bioactivity, which provides good bonding between tissues and the implanted materials, also necessary in most of the biological applications together with biocompatibility [7]. According to Kokubo and Takadama [8], bioactive materials form selectively bone-like hydroxyapatite when it is immersed into serum-like solution. Simulated body fluid (SBF) with ion concentrations nearly equal to human blood plasma can reproduce apatite in vivo [9]. Si₃N₄ is known as bioinert [6,10]; on the contrary, nowadays studies focused on the bioactivity of Si₃N₄ [10,11]. Si₃N₄ bioceramics have promising in vitro performance on the basis of reciprocity with living cells [12]. Production of composites with bioactive phases or surface coating with a hydroxyapatite layer promotes faster and stronger osseointegration and improves bioactivity of Si₃N₄.
Therefore, if highly densified Si$_3$N$_4$ ceramics could be produced and the performance of Si$_3$N$_4$ ceramics is improved, they will be good competitors to alumina or zirconia bioceramics with high fracture toughness, high strength, good wear-resistant, and high biocompatibility advantages.

Bioactive ceramics such as hydroxyapatite (HA) is known to have better osteoconductive potential than nearly bioinert ceramics [14]. HA is one of the major components of bone and tooth structure. The chemical similarity of human bone structure with HA makes it a preferred material for hard tissue applications. Although mechanical properties of HA are poor to be used as a monolithic form in hard tissue applications, it is a very good candidate to improve bone-bonding ability as a secondary phase in composites [9]. However, it is well known that the high-temperature sintering process causes dissociation of hydroxyapatite to biphasic calcium phosphate (BCP), i.e. a mixture of hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) and tricalcium phosphate (TCP, Ca$_3$(PO$_4$)$_2$) [15]. Nevertheless, the formation of TCP offers significant advantages for bone substitute materials because of its high biocompatibility and controlled degradability [16]. TCP has three polymorphs. β-TCP (rhomboedral) is a high-temperature phase that obtained above 650–750°C, and has two allotropic phases; α-TCP (monoclinic) above 1115–1150°C, and α’-TCP (hexagonal) above 1430–1470°C. α’-TCP to α-TCP reversion occurs immediately during cooling since α’-TCP is the only stable phase above high temperatures [17]. α-TCP has P2$_1$/a space group with lattice constants a = 12.887 Å, b = 27.280 Å, c = 15.219 Å, and β = 126.20° with 24 Ca$_3$(PO$_4$)$_2$ formula units (312 atoms) per unit cell. The bioactivity of α-TCP can be enhanced by dopants such as Si, Zn and Mg [18,19]. β-TCP has R3c space group with a = b = 10.439 Å, c = 37.375 Å, α = β = 90°, and γ = 120° with 21 formula units (273 atoms) per unit cell. Due to the uniform distribution of Ca vacancies, β-TCP becomes the most stable structure [20]. Moreover, β-TCP exhibits both osteoconduction and osteoinduction mechanisms and can be utilized as a bone-repairing material [21]. It is also known that β-TCP can stimulate the precipitation of the apatite layer in an aqueous ionic solution [22].

Graphene-based materials have been widely utilized in different ceramic systems to improve fracture toughness [23–32], tribological properties [33–35], oxidation resistance [30,31,36], and biocompatibility [37–39]. Furthermore, several studies [23,25,27,32,40–42] have been carried out to produce graphene-reinforced Si$_3$N$_4$ based ceramics. Ramirez et al. [23] have reported a fracture toughness of ~6.6 MPa·m$^{1/2}$ for highly densified (~99%) Si$_3$N$_4$-based composite with the addition of 4.3 vol% GNPs. Bodis et al. [25] have observed poor densification with the addition of MLG (multilayer graphene) into Si$_3$N$_4$. The authors reported a high fracture toughness of ~8.2 MPa·m$^{1/2}$ for the sample with 1 vol% MLG, but the density of this sample was only ~95%. Zhao et al. [26] have prepared GNPs reinforced BCP composites by hot pressing and evaluate the anisotropic mechanical properties. In another study, Si$_3$N$_4$ composites with 3 and 5 wt% GNPs were prepared by Tapasztó et al. [27] using spark plasma sintering. The authors reported a superior fracture toughness (~10.5 MPa·m$^{1/2}$) for Si$_3$N$_4$ with the addition of 3 wt% thin few-layer graphene nanoplatelets (FL-GNPs). Kvetkova et al. [32] have reported the Vickers hardness and fracture toughness for Si$_3$N$_4$-1 wt% GLP composite as ~16.4 GPa and 9.92 MPa·m$^{1/2}$, respectively, for which they did not specify the density. In most of the studies in the literature, high fracture toughness for monolithic Si$_3$N$_4$ or Si$_3$N$_4$-based composites were achieved with the formation of interlocking microstructure consisting of large elongated ~100% β-Si$_3$N$_4$ grains sintered with the additions of Al$_2$O$_3$, MgO, and rare earth oxides (Y$_2$O$_3$, CeO$_2$, etc.). Producing dense Si$_3$N$_4$ is difficult because of strong covalent bonding and low-self diffusion coefficients [43–45]. Si$_3$N$_4$ ceramics are commonly produced with the aid of additives which provide liquid phase sintering [43]. No-additive sintering can also be used as an alternative method to achieve dense Si$_3$N$_4$ [43–45]. In the present study, sintering processes were performed in the absence of additives not to deteriorate the biocompatibility of Si$_3$N$_4$. It is known that the sintering additives form liquid phase sintering and have a significant effect on the mechanical and tribological properties, and biocompatibility of Si$_3$N$_4$ based ceramics. Moreover, there are many results in the literature regarding the advantages of the production of Si$_3$N$_4$ ceramics using SPS [2]. Thus, different Si$_3$N$_4$-based ceramics were produced by this method; however, only a limited number of studies [243–46] focused on the processing of Si$_3$N$_4$ ceramics without using sintering additives.

The aim of this study is to produce highly dense Si$_3$N$_4$ based composites with good mechanical properties and bioactivity. In this paper, the effects of HA and HA-GNP additions on the properties of spark plasma sintered Si$_3$N$_4$ ceramics were systematically investigated in terms of phase analysis, microstructural development, mechanical properties, and in-vitro bioactivity behavior. Hydroxyapatite (HA) was added to Si$_3$N$_4$ to provide bioactivity. Although sintering additives were not used in this study, much higher densification and comparable to, or even higher amount of the β-Si$_3$N$_4$ phase formation were obtained for monolithic Si$_3$N$_4$ compared to some studies using sintering additives. The transformation of HA to TCP as a result of high-temperature sintering was not intentionally prevented for the HA-
containing composites to achieve the highest density with the best mechanical properties. Through the incorporation of GNPs into the Si$_3$N$_4$-HA composites, enhanced in-vitro bioactivity properties were achieved due to the formation of TCP phases.

2. Material and methods

2.1. Materials and sample preparation

Commercially available high purity silicon nitride (Si$_3$N$_4$, H.C. Starck, Grade M11-low oxygen; the impurity (wt%) information provided by the supplier is as follows: C: 0.1, O: 1.0, Fe: 0.003, Al: 0.05, Ca<0.01. The measured particle size is ~0.57 µm) was utilized as the matrix. Hydroxyapatite (HA, Sigma-Aldrich Chemical Co., USA, synthetic, purity: 99.8%. The measured particle size is ~20 µm) and graphene nanoplatelets (GNP, Nanokomp Co., Turkey, purity: >97, thickness: 5–8 nm, diameter: 5–10 µm) were used as secondary phases for composite preparation. Herein, Si$_3$N$_4$, Si$_3$N$_4$-HA, and Si$_3$N$_4$-HA-GNP composites were produced (Table 1). Si$_3$N$_4$-HA binary composite was developed with the addition of 5 vol% HA. The powders were weighed and mixed by wet ball milling for 24 h in a polyethylene bottle with Si$_3$N$_4$ balls and ethanol as a medium. For Si$_3$N$_4$-HA-GNP composites, the volume fraction of Si$_3$N$_4$ was kept constant at 95%, because the combination of maximum density and mechanical properties was achieved for this content in Si$_3$N$_4$-HA samples. Triple composites were prepared with 0.5–2 vol% GNP addition into binary composite having 95 vol% Si$_3$N$_4$. The GNPs were dispersed in ethanol using ultrasonic agitator. Then, Si$_3$N$_4$ and HA powder mixture slurry was added into the GNP suspension and dispersed again with an ultrasonic agitator (Hielscher UP400S, operating at 50% amplitude with on and off cycles) for 45 min. The powder mixtures in ethanol media were stirred until ethanol evaporated and dried in an oven at 105°C. The resulting powder was ground in an agate mortar.

For the SPS process, the graphite dies and punches were lined with a flexible graphite foil. Si$_3$N$_4$ and Si$_3$N$_4$-based powder mixtures were loaded into the die with an inner diameter of 50 mm to form a disc-shaped specimen with a thickness of ~4 mm. The sintering process was carried out using a spark plasma sintering (SPS) apparatus (7.40 MK-VII, SPS Syntex Inc.). The SPS temperatures of the samples were 1525°C and 1550°C, which depended on the second phase content (Table 1). An uniaxial pressure of 40 MPa and pulsed direct current (12 ms/on, 2 ms/off) were applied during the sintering process. The sintering was carried out with a heating rate of 120°C/min in a vacuum with a holding time of 5 min at sintering temperatures.

2.2. Characterization of samples

The densities of the Si$_3$N$_4$-based samples were measured by the Archimedes method in accordance with ASTM B-311-13 procedure. Although the exact volume fraction of phases (except for Si$_3$N$_4$) was not known, the approximate relative densities can be estimated since very close theoretical densities of Si$_3$N$_4$ (3.18 g/cm$^3$), HA (3.16 g/cm$^3$), β-TCP (3.07 g/cm$^3$) and α-TCP (2.86 g/cm$^3$) [26,47]. Phase analysis of the Si$_3$N$_4$-based sintered samples was performed by XRD (MiniFlex, Rigaku Corp. and Philips PANalytical X’Pert Pro) with CuKα radiation at 30 kV and 15 mA over a 2θ range of 20–80° with 0.02° steps. Micro-Raman spectroscopy (Bruker SENTERRA) was utilized to confirm the existence of GNPs after the SPS process. Microstructural characterization was conducted on a field emission gun scanning electron microscope (FEG-SEM, JEOL JSM 7000 F). The Vickers hardness and indentation fracture toughness were evaluated by Vickers indentation technique (VHMOT, Leica Corp.) at room temperature under loads of 9.8 N and 19.6 N, respectively. The indentation fracture toughness was determined from the half-length of a crack formed around the indentations [19]. More than 10 indentations were made for each sample. SPS is a pressure-assisted sintering technique, and during SPS, GNPs are preferentially oriented perpendicular to the pressure direction. The fracture toughness of GNP-containing samples was measured along two directions: the direction parallel (cross-plane, designated by //SPS) and perpendicular (in-plane, designated by ⊥SPS) to the SPS pressing axis.

The in vitro bioactivity of Si$_3$N$_4$, Si$_3$N$_4$-HA and Si$_3$N$_4$- HA-GNP composites was investigated by soaking the samples in a simulated body fluid (SBF), which was prepared according to Kokubo’s procedure [48]. The temperature of the solution was kept constant at 37°C during the test, which was performed under the nitrogen atmosphere with dynamic conditions (~80 rpm). The samples were removed from the solution after 1, 7, 14, 21 and 28 days, washed with deionized water and dried in an oven. The morphology of the precipitated layer on the surface of the samples depending on the soaking time and composition of the sample were examined using FEG-SEM with energy-dispersive spectroscopy (EDS) attachment (Oxford Instrument, INCA).

3. Results and discussion

3.1. Densification behavior and phase evolution

Bulk and relative densities of the spark plasma sintered samples are given in Table 1. The density
Table 1. Composition, relative density, hardness, and fracture toughness of the spark plasma sintered specimens.

| Si$_3$N$_4$ | HA | CWP | Sample code | Sintering temperature (°C) | Bulk density (g/cm$^3$) | Relative density (%) | Vickers hardness (GPa) | Fracture toughness (MPa·m$^{1/2}$) | Density | Hardness | Toughness |
|------------|----|-----|-------------|---------------------------|-------------------------|----------------------|----------------------|-------------------------------|---------|----------|-----------|
| 100        | 90 | 90  | M4          | 1525                      | 3.17                    | 99.7                 | 13.7 ± 0.16           | 113 ± 0.66                   | 1525    | 4.5      | 3.16      |
| 100        | 90 | 90  | 5.0GP       | 1525                      | 3.16                    | 99.9                 | 13.49 ± 0.26          | 1297 ± 0.26                 | 1525    | 4.78     | 4.75      |
| 100        | 90 | 90  | 5.0GP       | 1525                      | 3.16                    | 99.9                 | 13.49 ± 0.26          | 1297 ± 0.26                 | 1525    | 4.78     | 4.75      |
| 100        | 90 | 90  | 1.5GNP      | 1525                      | 3.16                    | 99.9                 | 13.49 ± 0.26          | 1297 ± 0.26                 | 1525    | 4.78     | 4.75      |
| 100        | 90 | 90  | 1.5GNP      | 1525                      | 3.16                    | 99.9                 | 13.49 ± 0.26          | 1297 ± 0.26                 | 1525    | 4.78     | 4.75      |
| 100        | 90 | 90  | 1.5GNP      | 1525                      | 3.16                    | 99.9                 | 13.49 ± 0.26          | 1297 ± 0.26                 | 1525    | 4.78     | 4.75      |
| 100        | 90 | 90  | 3.5GNP      | 1525                      | 3.16                    | 99.9                 | 13.49 ± 0.26          | 1297 ± 0.26                 | 1525    | 4.78     | 4.75      |
| 100        | 90 | 90  | 3.5GNP      | 1525                      | 3.16                    | 99.9                 | 13.49 ± 0.26          | 1297 ± 0.26                 | 1525    | 4.78     | 4.75      |
| 100        | 90 | 90  | 3.5GNP      | 1525                      | 3.16                    | 99.9                 | 13.49 ± 0.26          | 1297 ± 0.26                 | 1525    | 4.78     | 4.75      |
| 100        | 90 | 90  | 3.5GNP      | 1525                      | 3.16                    | 99.9                 | 13.49 ± 0.26          | 1297 ± 0.26                 | 1525    | 4.78     | 4.75      |

Measurements revealed that the densities of Si$_3$N$_4$-based samples varied between ~89 and ~99% of the theoretical density. The highest values were obtained for Si$_3$N$_4$ and composites with small amounts of secondary phase additions. The SPS temperature had a significant effect on the density and formation of phases for Si$_3$N$_4$: at 1350°C, the relative density of Si$_3$N$_4$ was only ~89%, with increasing SPS temperature to 1550°C, the density of the sample increased to over 99%. This agrees with previous studies [49–52]. On the other hand, the density of Si$_3$N$_4$ measured herein is higher than that of some reported results in the literature [2,40,46,53,54]. Ratzker et al. [2] have stated that although 500 MPa pressure was applied during spark plasma sintering, they achieved only ~67% relative density for Si$_3$N$_4$ without using sintering additives. Ceja-Cardenas et al. [46] have prepared spark plasma sintered Si$_3$N$_4$ without using sintering additives and reported a very low relative density, ~65%. Saleem et al. [40] have reported a relative density of ~96.5% for hot-pressed Si$_3$N$_4$, although they used sintering additives. Miyazaki et al. [53] have achieved the highest relative density as ~98.4% for Si$_3$N$_4$ with 1 mol% MgO and 7 mol% Yb$_2$O$_3$. The differences in densities could be attributed to the characteristics of the starting powder and processing technique. Herein, a high-density Si$_3$N$_4$ was achieved without using sintering additives. This could be attributed to the presence of impurities in starting powder of Si$_3$N$_4$. Tanaka et al. [43] and Homma et al. [55] have investigated the sintering behavior of Si$_3$N$_4$ powders with different impurity levels. They reported higher sintering temperatures for full densification for higher purity powder. The densification of Si$_3$N$_4$ is highly sensitive to sintering conditions and the composition of the sintering atmosphere [1]. The starting Si$_3$N$_4$ powder contains SiO$_2$. Moreover, carbon is present from the graphite foil, dies and punches that are used during SPS. Additionally, GNP are another carbon source for ternary composites. The carbothermal reduction of SiO$_2$ and removal of oxygen impurities from the structure might have prevented the entrapment of pores and caused nearly full densification of Si$_3$N$_4$. Due to the vacuum atmosphere of SPS, equation (1) becomes favorable at significantly lower temperatures, and CO$_{(g)}$ and SiO$_{(g)}$ were removed from the chamber. Hence, due to under very high partial pressure of SiO$_{(g)}$, Si$_{(s)}$ and SiO$_2(s)$ formed with disproportional reaction given in equation (2) [56].

$$\text{SiO}_2(s) + C(s) \rightarrow \text{SiO}_1(g) + \text{CO}_1(g)$$

$$2\text{SiO}_1(g) \rightarrow \text{Si}_1(s) + \text{SiO}_2(s)$$

Figure 1 shows the XRD patterns of starting powder of HA, Si$_3$N$_4$ before sintering and Si$_3$N$_4$ based samples after sintering at 1525–1550°C. The phase analysis revealed that the starting Si$_3$N$_4$ powder mainly
composed of α-Si₃N₄, although the characteristic peaks of β-Si₃N₄ were also detected (Figure 1a). The peaks in XRD patterns were indexed as α-Si₃N₄ (JCPDS no. 41–0360), β-Si₃N₄ (JCPDS no. 33–1160) and HA (JCPDS no. 9–0432). The weight fraction of β-Si₃N₄ was calculated by using the intensity of the two highest peaks of β-Si₃N₄ and α-Si₃N₄ [57]. For calculation of α/β-Si₃N₄ phase ratio for starting powder, peaks belonging to (201) and (210), and (101) and (210) were selected for α-Si₃N₄ and β-Si₃N₄, respectively. The calculation suggested that the starting powder consisted of 86.46 wt% α-Si₃N₄ and 13.54 wt% β-Si₃N₄. The XRD pattern (Figure 1b) of Si₃N₄ sintered at 1550°C suggested that although some peaks of α-Si₃N₄ phase were detected, the sample was mostly composed of β-Si₃N₄. For calculation of α/β-Si₃N₄ phase ratio for the sample (Figure 1b), peaks corresponding to (222) and (330), and (101) and (210) were selected for α-Si₃N₄ and β-Si₃N₄, respectively. The β-Si₃N₄ phase content was ~87 wt% for all sintered samples of Si₃N₄. 5 HA, 1 GNP and 2 GNP.

XRD analysis of 5 HA (Figure 1d) revealed the formation of β-Si₃N₄ phase and complete phase transformation from HA to β-TCP (β-Ca₃(PO₄)₂), and α-TCP (α-Ca₃(PO₄)₂) as a secondary phase after SPS at 1525°C. Fernandez et al. [58] have reported α-TCP, β-TCP and iron formation of iron-modified α-TCP after sintering at 1400°C. Reid et al. [59] have stated that Mg raises the β-TCP thermal stability to ~1400°C. The sintering of HA at high temperatures resulted in the elimination of the functional hydroxyl group in Ca₁₀(PO₄)₆(OH)₂ and decomposition of HA into α-TCP, β-TCP, CaO [60] and tetra-calcium phosphate (TTCP) [61]. At ~1500°C, related to the TCP phase transition temperatures, it is expected to observe only α-TCP phase. However, β-TCP is the primary phase in Si₃N₄-based composites after sintering. This could be related to the chemical composition and physical properties of the starting materials. In the presence of impurities, TCP phase transition temperatures can vary over a broad range [62]. Moreover, aggressive supercooling is required to avoid the formation of β-TCP (equilibrium phase) upon cooling to room temperature [63]. Due to the nature of SPS, aggressive supercooling is not possible and thus the formation of β-TCP phase is not suppressed. The characteristic peaks of β-TCP (JCPDS no. 9–016) at 2θ = 27.7°, 31.0°, and 34.3° corresponding to the (214), (0210), and (220) planes, respectively, were detected in all sintered samples. 5 HA also contained a very small amount of α-TCP as evidenced by a very-low-intensity set of peaks around 2θ = 31.7° matching with the characteristic peak position of α-TCP (JCPDS no. 9–0348). Sayer et al. [18] have reported that in the presence of SiO₂, silicon stabilized tricalcium phosphate (SiTCP) is formed within the HA-TCP system when stoichiometric precipitate of hydroxyapatite is sintered at 1000°C. The formation of α-TCP in 5 HA samples could be related to the formation of the SiTCP phase. SiTCP has a monoclinic structure with a space group P2₁/a similar to α-TCP

![Figure 1](image_url)

Figure 1. XRD patterns of (a) Si₃N₄ starting powder, (b) 100S sintered at 1550°C, (c) HA starting powder, (d) 5 HA, (e) 1 GNP, and (f) 2 GNP.
distinguished from α-TCP by its lattice constants 

\( a = 12.863 \pm 0.004 \text{ Å}, \ b = 9.119 \pm 0.003 \text{ Å}, \ c = 15.232 \pm 0.004 \text{ Å}, \ \beta = 126.3 \pm 0.1^\circ \) and the formation temperature [18]. Si₃N₄ starting powder includes oxide impurities which tend to form the Si-TCP phase. Silicon dissolves in HA structure, and P⁵⁺ substitutes by Si⁴⁺ to form holes on the OH⁻ sites that initiate the transformation to Si-TCP [18,64].

Similarly, in phase analysis of GNP added composites (Figure 1e and f), HA decomposed to β-TCP and α-TCP phases during the high-temperature sintering process. The same characteristic peaks of β-TCP were also detected in both 1GNP and 2GNP. In addition to \( 2\theta = 31.7^\circ \) matching with the characteristic peak position of α-TCP, additional peaks were detected at \( 2\theta = 32.7^\circ \) and \( 2\theta = 20.4^\circ \) for 1GNP and 2GNP, respectively. Although HA content decreases with increasing GNP content, phase intensities for 2GNP (Figure 1f) were higher than that of 1GNP. This could be the result of the oxygen removal mechanism through equation (1) and (2). Increasing carbon content in the system might trigger the disproportional reaction and result in the formation of more SiO₂. Accordingly, increasing SiO₂ content favors the decomposition of HA into β-TCP and α-TCP [64].

5 HA had a bulk density of 3.17 g/cm³, which indicated high densification. It was observed that (not given) density decreased with increasing HA content. The limited densification at high HA loading (10 and 15 vol%) could be attributed to HA decomposition. The dehydroxylation of HA produces water, which causes volume expansion. When water evaporates, it leaves behind pores according to the following equation (3) [60]:

\[
\text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 \rightarrow \text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 - 2x\text{O}_x \text{V}_x + x\text{H}_2\text{O} \uparrow
\]

The dehydroxylation process is followed by the decomposition to oxyapatite and tricalcium phosphate according to the following equation (4) [60]:

\[
\text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 \rightarrow 2\text{Ca}_3 (\text{PO}_4)_2 + \text{Ca}_4 \text{P}_2 \text{O}_9 + \text{H}_2\text{O} \uparrow
\]

This decomposition leads to a reduction in mechanical properties [60,65]. Ou et al. [60] have reported a decrease in density for pure HA when sintered at high temperature. The authors explained this phenomenon by the existence of nanotubes caused by the formation of TCP phases in HA, which was considered as the main reason for low density.

The volume fraction of the matrix phase (Si₃N₄) was kept constant at 95% for GNP-containing samples. Since the formation of β-TCP and α-TCP, the bulk density of the ternary composites was considered. The best densification (~99%) was achieved for the samples 0.5GNP and 1GNP. On the other hand, 1.5GNP and 2GNP showed poor densification as compared to the 0.5GNP and 1GNP. This could be related to the formation of more α-TCP, which has a lower density (2.86 g/cm³) than that of β-TCP. A similar adverse effect of GNP on densification behavior was also reported for hot-pressed Si₃N₄-GNP and spark plasma sintered Al₂O₃-GNS (graphene nanosheet) composites, respectively [40,66].

3.2. Raman analysis

The structures of pure GNPs and the triple composites with 1 and 2 vol% GNPs after sintering were investigated by micro-Raman spectroscopy over the range of 1100−2800 cm⁻¹ as given in Figure 2. The characteristic Raman peaks of GNPs were analyzed at the fractured surfaces of the samples. Raman spectra from the pure GNPs and composites exhibited the presence of D (~1350 cm⁻¹), G (~1582 cm⁻¹) and 2D (~2700 cm⁻¹) peaks in the positions, which confirmed the retention of the 2D structure of graphene after sintering at 1525°C. The Raman spectra of the samples (Figure 2b and c) showed broadened and asymmetrical peaks in comparison to that of GNP powder (Figure 2a). This is an indication of the presence of the multi-layered structure of graphene [67], as shown by microstructural characterization as well.

The D and 2D peaks in sintered samples were red-shifted, while the G peak was blue-shifted (Figure 2b and c). Doping of graphene always causes a shift of the G and 2D peaks positions due to electron–phonon coupling. The 2D band of graphene is the most sensitive peak to electronic and phonon band-structure changes [68]. For 2D band, electron doping and tensile strained graphene caused redshift [69]. Similarly, increasing temperature, which changes phonon frequency, also red-shifts the 2D band [70]. In the planes of 2D materials with high symmetry, the mechanical, thermal, optical and electric properties are isotropic. However, the reduction in lattice symmetry induces in-plane anisotropy in these properties due to crystalline orientation [71]. The anisotropy of the graphene lattice under strain, which was proven in this study by the GNP aligning in an in-plane direction (Figure 4), and symmetry breaking could be the reason for the redshift of the D band [72]. Increasing GNP amount from 1 to 2 vol% caused narrowed and upshifted G band (Figure 2b and c). This is the indicator of compressive strain due to both electron and hole doping [69]. The position and shape of the G band are strongly affected by the defect density and thermal residual stresses. Moreover, the intensity ratio of the D-band to G-band (I_D/I_G) is used to measure defect density. The composites gave increased D peak intensities
and, as a result, the intensity ratio of I_D/I_G increased from ~0.1 to ~1.1 for the pure GNPs and samples, respectively. The high-intensity ratio of D/G confirmed that the ball-milling, ultrasonic agitation and/or SPS process caused the formation of substantial amounts of defects in the GNPs in composite structures.

### 3.3. Microstructural characterization

Figure 3 shows the fracture surface micrographs of 100S sintered at 1550°C. The microstructural characterization is consistent with the density measurements and XRD analysis. The fracture surface of the sample showed a dense microstructure and Si₃N₄ grains exhibited mainly transgranular fracture. Besides, the specimen sintered at 1550°C showed the formation of elongated β-Si₃N₄ grains (indicated by a dotted line in Figure 3b). The content of β-Si₃N₄ was measured as ~87 wt% from the XRD analysis of 100S (Figure 1b). However, it is clear from the microstructure that the amount of elongated β-Si₃N₄ is lower than ~87 wt%. This might be an indication of the existence of equiaxed-shaped β-Si₃N₄ grains. Above the melting temperature of SiO₂ (1710°C), the rate of β-Si₃N₄ formation is high [1], and grains tend to elongate as a result of the solution-precipitation sequence [43]. On the other hand, equiaxed-shaped β-Si₃N₄ grains form when α to β transformation occurs without a liquid phase [43]. Moreover, α-Si₃N₄ phase remained in the microstructure as detected in XRD analysis (Figure 1b). In the microstructure, a few cleavage planes (indicated by yellow arrows in Figure 3c) were also observed, but they were not enough to have a detrimental effect on the fracture toughness of the sintered Si₃N₄.

The fracture surface microstructure analysis of 5 HA (Figure 3d) suggested that the sample showed high density. Note in Figure 3d that fine CaPO₄-based particles (white) were seen. The calcium to phosphorus (Ca/P) molar ratio was determined as 1.52 from the EDS analysis (Figure 3e and f). This value also confirms the presence of β-TCP and α-TCP phases in the microstructure.

Figure 4 shows the fracture surfaces of sintered Si₃N₄-HA-GNP composites. All samples showed a high-density microstructure. The fracture surfaces of the composites revealed an intergranular fracture mode. Elongated β-Si₃N₄ grains can be detected easily from Figure 4b and 4d (indicated by the white dotted line) and Figure 4f. Moreover, finer grains of the matrix can be observed from the fracture surface micrograph of a triple composite with 2 vol% GNPs (Figure 4h). The high magnification SEM images show that GNPs retain their platelet shape after consolidation. The graphene layers were strongly kept together by Van der Waals forces, so a large agglomerated GNPs appeared at high GNPs loading. Figure 4g shows agglomerated and overlapped platelets with ~10 μm in length and ~3 μm in thickness (indicated by the yellow dotted line).

![Figure 2](ImageDescription) Raman spectra of the (a) pristine GNPs, (b) 1GNP, and (c) 2 GNP after sintering at 1525°C. Insets show the detailed Raman spectra shift of G and 2D bands.
When the length and thickness of overlapped GNP were larger than the matrix grain size, the grain refinement effect of GNP might be weak. In addition, the gap formation was observed at the matrix and GNP interface, which may serve as a stress concentrator, and lower the mechanical properties. A similar feature was also reported for the Al$_2$O$_3$-MLG systems [73].

Moreover, GNPs were aligned in an orientation perpendicular to the pressing axis of SPS (indicated by the yellow arrows in Figure 4c and g). This alignment behavior of graphene during the SPS process agrees with previously reported studies [28,29,42,74]. Figure 4b and 4d show the bending-kinking and sliding of GNPs, respectively. They are known as intrinsic energy dissipation mechanisms. The bending of GNPs originated from the exposure of pressure during the SPS process was also observed (Figure 4d).

### 3.4. Mechanical properties

The Vickers hardness and indentation fracture toughness of Si$_3$N$_4$ and Si$_3$N$_4$-based samples are summarized in Table 1. The microhardness measurements were conducted on polished sample surfaces parallel with the SPS pressing direction. The average Vickers hardness of Si$_3$N$_4$ was ~17.6 GPa. A similar result (~17.5 GPa) was reported by Tapaszo et al. [27] who studied spark plasma sintered Si$_3$N$_4$. On the other hand, Walker et al. [28] have reported a Vickers hardness of ~22.3 GPa, which is higher in comparison with the results of the present study. This high hardness could be attributed to the presence of ~100% α-Si$_3$N$_4$ phase. It is known that α-Si$_3$N$_4$ has higher Vickers hardness than that of β-Si$_3$N$_4$ [1]. The moderate hardness obtained herein could be attributed to the presence of ~13 wt% α-Si$_3$N$_4$ and high densification after SPS at 1550°C. The microhardness of 5 HA was measured as ~13.8 GPa. The Vickers hardness of binary composite was significantly lower than that of sintered Si$_3$N$_4$ (~17.6 GPa). The highest hardness was obtained as ~13.5 GPa for 0.5GNP among all the Si$_3$N$_4$-based composites. ~18% decrease was observed in the Vickers hardness of the Si$_3$N$_4$-HA-GNP samples with increasing GNP content up to 2 vol%. The lower hardness of 1.5GNP and 2GNP compared to the others can be explained by the residual porosity that remains in the samples after sintering at 1525°C which is consistent with the density results (Table 1). The amount of porosity increased up to ~6% in 2GNP sample. In brief, herein, two possible reasons are considered for the decrease in Vickers hardness with the addition of HA: as a result of decomposition of HA (i) the presence of softer and less dense TCP phases in comparison to the Si$_3$N$_4$ matrix, (ii) the formation of nanopores. Ou et al. [60] have reported density and hardness reduction for HA compacts that held at 1400°C by the formation of nanopores as a consequence of transformation of β-TCP to α-TCP. Previously, several studies have reported Vickers hardness of TCP phases as ~2.24 GPa for both β-TCP, and α-TCP included laminates sintered at 1200°C [75] and ~4.57 GPa for BCP sintered at 1300°C [76]. For GNP added composites, in addition to HA decomposition, the presence of pores could be attributed to the agglomeration and overlapping of GNPs (with a thickness of ~1 μm) as observed in SEM micrographs (Figure 4g). Flexibility of aggregated GNPs decreased, which resulted in the formation of extra pores [40]. Approximately 2% decrease in relative density with
the addition of GNPs (0.5–2.5 wt%) was reported by Zhao et al. [26] for hot-pressed biphasic calcium phosphate-GNPs system. Similarly, Saleem et al. [40] have reported a decrease in bulk density for hot-pressed Si₃N₄-GNP composites.

The indentation fracture toughness of the samples is presented in Table 1 as a function of composition. The fracture toughness of 100S was measured as ~5.8 MPa·m¹/². Although this result is higher than that of some reported values [27,52] in the literature, it is also lower than the others. For example, Balazsi et al. [52] have reported a fracture toughness of ~5.2 MPa·m¹/² for the spark plasma sintered Si₃N₄ with the additions of 4 wt% Al₂O₃ + 6 wt% Y₂O₃. Tapasztó et al. [16] have also reported a lower fracture toughness (~5.1 MPa·m¹/²) and Vickers hardness (~17.5 GPa) for the spark plasma sintered Si₃N₄ with 6 wt% Al₂O₃ + 4 wt% Y₂O₃ than that of the present study. Moreover, Bodis et al. [25] have studied the spark plasma sintering of Si₃N₄ with 4 wt% Al₂O₃ + 6 wt% Y₂O₃. The reported results of Vickers hardness and fracture toughness were ~18.3 GPa and ~6.3 MPa·m¹/², respectively. On the other hand, Tiegs et al. [77] have reported superior indentation fracture toughness of ~7.5 to ~8.4 MPa·m¹/² for Si₃N₄ with additives of Y₂O₃ and Al₂O₃, which was produced by gas pressure sintering (GPS). It is known that the optimization of size and aspect ratio of β-Si₃N₄ grains is critical for improved mechanical properties. The microstructure should consist of a high amount of high-aspect-ratio β-Si₃N₄ grains to achieve high fracture toughness and strength [1]. However, Saleem et al. [40] have reported a lower Vickers hardness, ~15.3 GPa, and a moderate fracture toughness of ~5 MPa·m¹/² for hot-pressed Si₃N₄.
although they determined complete transformation from α-Si$_3$N$_4$ to β-Si$_3$N$_4$. In a different work, Dusza et al. [41] have reported a low Vickers hardness of ~15.4 GPa, but high fracture toughness of 6.9 MPa·m$^{1/2}$ for hot isostatic pressed Si$_3$N$_4$ with additives of Al$_2$O$_3$, Y$_2$O$_3$, and ZrO$_2$. The decrease in hardness and an increase in fracture toughness may be explained by the presence of mainly the β-Si$_3$N$_4$ matrix. Bocanegra-Bernal et al. [78] have summarized indentation fracture toughness of Si$_3$N$_4$-based ceramics. Accordingly, the difference in mechanical properties in different studies could be attributed to the type and amount of additives, sintering conditions, and the presence of elongated grains in the microstructure [78]. The fracture toughness decreased by ~3.5 with the addition of 5 vol% HA into Si$_3$N$_4$. The reported indentation fracture toughness of β-TCP (~1.3 MPa·m$^{1/2}$) is higher than that of hydroxyapatite (~0.9 MPa·m$^{1/2}$) [79,80]. Therefore, herein, as a result of the transformation of HA to TCP, a tougher phase formed in the microstructure as compared to the case of HA. Moreover, low HA loading, dense and fine-grained microstructure can explain why no significant change in fracture toughness occurs by the incorporation of 5 vol% HA into Si$_3$N$_4$. Figure 5 shows the crack paths generated by the Vickers indentation tests. A tortuous crack path was observed for 100S (Figure 5a) and 5 HA (Figure 5b). It is obvious that there is a strong crack propagation resistance, and crack deflection plays an important role in improved fracture toughness. Ye et al. [81] have observed similar crack propagation paths for Si$_3$N$_4$-based composites.

The fracture toughness of GNP-containing samples tested in both directions (cross-plane: // to SPS pressing axis and in-plane: ⊥ to SPS pressing axis) are given in Table 1. It is clear that in-plane fracture toughness results were higher than that of cross-plane. The fracture surface microstructures revealed that GNPs were aligned mostly in a direction perpendicular to the SPS pressing axis (in-plane direction, Figure 4) during the consolidation, and this preferential orientation of GNPs introduced an anisotropy in fracture toughness. It is known that the mechanical properties of cortical bone are also anisotropic. The anisotropy induced by 0.5 and 1 vol% of GNPs was strong. The difference between the cross-plane and in-plane fracture toughness was determined as ~26% and ~24% for 0.5GNP and 1GNP, respectively. The preferential orientation of GNPs can enhance the fracture toughness of GNP-containing samples. However, the addition of GNP into binary composites did not cause an increment in fracture toughness. It increased (~5.9 MPa·m$^{1/2}$) by ~2% with the incorporation of 1 vol% GNPs into a binary composite. Moreover, a further increase in GNPs content caused a decrease in fracture toughness in both directions. The decrease in fracture toughness could be attributed to the weak interfacial bonding between the GNPs and Si$_3$N$_4$ grains when the GNP loading was greater than 1 vol%.

The crack deflection, which can consume crack propagation energy was observed for 0.5GNP (Figure 5c). The propagation of cracks at 1GNP (Figure 5d) is mostly in a zig-zag route, which indicates a strong interfacial bonding. Micrographs and the mechanical property data obtained herein suggest that the main toughening mechanisms for the GNP-containing samples are considered as pull-out (Figure 4) and crack deflection in the in-plane and cross-plane directions. However, the overlapped and agglomerated GNPs were observed (Figure 4) even at the lowest GNP loadings (0.5 vol%, Figure 4b). The thick platelets reduced the flexible character of GNPs and caused the formation of localized porosity, which serve as crack initiation sites [30,31,82]. The effectiveness of toughening mechanisms may be reduced by the formation of thick GNPs.

### 3.5. In-vitro bioactivity characterization

The in-vivo integration ability of an implant can be predicted by the apatite formation capability on the surface in SBF. The formation of apatite-like phase on the sample surface might be beneficial for differentiating the maturation of osteoblasts, cell adhesion and proliferation [21]. Figure 6 shows the surface morphologies of the monolithic Si$_3$N$_4$, Si$_3$N$_4$-HA and Si$_3$N$_4$-HA-GNP composites after soaking in SBF for 14 and 28 days. 0.5GNP and 1GNP were selected to determine the effect of GNP addition on in vitro bioactivity behavior because these samples achieved the combination of highest densification and best mechanical properties. After 1, 7 and 14 days (Figure 6a), no calcium phosphate-based particles formed on the surface of 100S. After 7 and 14 days, small calcium phosphate-based particles with a diameter of ~1-3 μm grew on the surface of 5 HA (Figure 6c). After 21 days, calcium phosphate-based particles with a diameter of ~10-20 μm and ~20-50 μm formed on the surface of 100S and 5 HA, respectively. After 28 days, calcium phosphate-based particles with a diameter of ~30-80 μm formed on the surface of 5 HA, however, they did not form a continuous layer (Figure 6d). Contrary to expectations, a trace of calcium phosphate-based particles with a diameter of ~20-50 μm formed on 100S after 28 days (Figure 6b). At the molecular level, all bioceramics completely interact with living tissue that may improve performance and implant lifetime by stimulating cells to replicate and function with exceptional efficiency in spite of
wholly bioinert nature [12]. Precipitate formation shows that silicon nitride is a bioinert material with a good biological response [6]. Neumann et al. [83] have reported as a result of in vitro studies that Si$_3$N$_4$ has good osseointegration and biocompatibility as Al$_2$O$_3$.

Granules composed of many small spherical crystallites were observed from high magnification images (insets in Figure 6c-f) of the composites. This spherulite morphology is related to the high nucleation rate of phosphorus and calcium and was observed for all samples after 28 days of immersion in the present study. Similarly, small granular structure formation on the (HA)/Ti-6Al-4V composite coatings after 14 days soaking in SBF [84], large spherulites on the surface of Bioglass-HA composites after 7 days SBF soaking [85], and hemispherical granular precipitates on the surface of the β-TCP sample after 7 days of immersion in SBF [86] were reported.

Currently, researches are focused on the mixture of calcium phosphates that contain the most stable phases of HA and the soluble phases of TCP, due to the non-resorbable nature of HA. The calcium and phosphate ions, which act as a seed in new bone formation release into the biological medium [87]. Synthesizing the highly biodegradable calcium phosphates is a challenge. Previously, Li et al. [88] have synthesized highly biodegradable biphasic tricalcium phosphates (BTCP) composed of α-TCP and β-TCP, since the α-TCP degradation rate is much higher than that of β-TCP [89]. The EDS analysis was conducted to determine the chemical composition of precipitates on the surface of the samples. Ca/P molar ratios were lower than that of stoichiometric HA (1.67) and calculated as 1.56, 1.52 and 1.44 for 5 HA, 0.5GNP and 1GNP, respectively. This is the indication of the appearance of both HA and TCP phases. β-TCP has two repeating planar domains with Ca/P ratios 1.429 and 1.571. Also, 1.443 was reported as the Ca/P ratio of β-TCP [62]. XRD analysis could not be performed and the total amount of precipitates could not be detected since there was no continuous layer formation on the surface.

The microstructural characterization results indicated that the formation of spherulite calcium phosphate-based particles was improved with the addition of GNPs compared to the 5 HA (Figure 6). Moreover, herein, the size of the precipitates increased and they tended to coalesce when the soaking duration increased from 7 to 28 days. Rapid formation of spherical apatite layer and improved in vitro bioactivity character were reported by Zhao et al. [90] for graphene oxide (GO) coated quartz substrate after soaking in SBF.

Figure 5. SEM images of the indentation crack paths in the polished surfaces of (a) 100S, (b) 5 HA, (c) 0.5GNP, and (d) 1GNP. Note the magnifications are different. The yellow arrows indicate crack deflection.
for 14 days. Zhang et al. [38] have reported a thicker apatite layer formation after 7 days of immersion in SBF for 1 wt% graphene nanosheet (GNS) containing HA-GNS composite. Basirun et al. [39] have reviewed the same phenomenon and claimed that the existence of GNPs makes the sample surfaces appropriate for bone-like apatite formation. After 1 day, no calcium phosphate-based particles formed on the surfaces for both 0.5GNP and 1GNP. For 0.5GNP, the size of calcium phosphate-based particles was in the ranges of ~1-5 µm, ~8-80 µm, ~60-140 µm, and ~100-350 µm after SBF soaking times of 7, 14, 21 and 28 days, respectively. For 1GNP, after 7, 14, 21 and 28 days, ~2-8 µm, ~15-90 µm, ~110-250 µm, and ~550 µm sized calcium phosphate-based particles formed, respectively. The addition of GNPs increased the amount of both β-TCP and α-TCP phases. Larger calcium phosphate-based particle formation for GNP-containing samples could be related to the presence of α and β-TCP phases. Juhasz et al. [91] have reported the formation of small apatite crystals, when they inserted TCP in SBF. Moreover, according to equation (2), SiO₂ and Si formed with the addition of GNP into the system. SiO₂ added HA performs superior bioactivity than that of pure HA in SBF [92]. Also, reaction product silicon increases the bioactivity of α-TCP [93].

TCP is an ideal temporary scaffold used for bone replacing autogenous bone due to its close chemical nature to biological apatite in human hard tissues [94]. β-TCP polymorph is highly biocompatible, biodegradable, and commonly used in orthopedic applications as bone substitutes due to its bone generation ability. Furthermore, bioactivity behavior

**Figure 6.** SEM microstructures of 100S after (a) 14 and (b) 28 days, 5 HA after (c) 14 and (d) 28 days, 0.5GNP after (e) 14 and (f) 28 days, 1GNP after (g) 14 and (h) 28 days of immersion in SBF. Note the magnifications are different.
of α-TCP, microstructural and chemical resemblance of its hydration products to the bone make this polymorph potential candidate for hard tissue applications [95]. Further investigations, such as cell viability, bacterial studies, or cytotoxicity are required. However, experimental results indicate that the Si₃N₄ based samples with TCP phases and GNPs have mechanical properties that are comparable with those of currently used in implant systems.

4. Conclusions

Herein, Si₃N₄ ceramics without using sintering aids, Si₃N₄-HA and Si₃N₄-HA-GNP based composites were produced by SPS at 1525–1550°C under 40 MPa for 5 min. The resulting samples have relative densities of ~94 to ~99%. Almost full densification (~99%) and a high amount of β-Si₃N₄ (~87 wt%) formation were achieved for Si₃N₄ after sintering at 1550°C without sintering additives. The relative density of Si₃N₄ decreased with increasing HA content in starting powder. The achieving of limited densification with the incorporation of HA could be attributed to HA decomposition and formation of the TCP phases, specifically α-TCP phase, in the microstructure after sintering.

The addition of GNPs into Si₃N₄-based composites did not cause a significant improvement in fracture toughness. This could be attributed to the formation of overlapped and agglomerated GNPs. The 1GNP had the highest fracture toughness of ~5.9 MPa·m⁰·⁰. The main toughening mechanisms that originated from the presence of the GNPs were determined as pull-out and crack deflection in the in-plane and cross-plane directions.

GNP addition contributed to the formation of TCP phases, accordingly, the GNP-containing samples exhibited better bioactivity.

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