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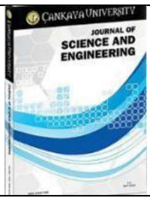

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Hydroxyapatite Deposition on Silicon Nitride and SiAlON Ceramic Substrates via Biomimetic Method

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Keywords

Silicon Nitride,
SiAlON,
Biomimetic Coating

Abstract

Silicon Nitride (Si_3N_4) ceramics hold significant promise as materials for biomedical implants, but their biocompatibility and osseointegration performance can still be improved to improve host tissue-implant interaction. One approach to improve interaction involves the application of a Hydroxyapatite (HAp) $Ca_{10}(PO_4)(OH)_2$ coating. Various techniques, including solid-state reactions, hydrothermal methods, sol-gel processes, and biomimetic approaches, have been employed for this purpose, achieving partial success in mimicking bone-like apatite formation. Biomimetic coating, among these methods, is particularly valuable for enhancing the biocompatibility of different orthopedic implants. It can be applied not only to ceramics but also to materials featuring active chemical groups on their surfaces, such as metals and organic polymers, which serve as nucleation sites for mineralization. In this study, Si_3N_4 and SiAlON ceramics were compared regarding their potential to deposit hydroxyapatite in simulated body fluid (SBF) with varying concentrations. The apatite layers formed on the surfaces after immersion in 1.5 SBF were analyzed using a Scanning Electron Microscope (SEM) and energy-dispersive X-ray (EDX) analysis. Consequently, Ca/P ratios matching non-stoichiometric biological apatite values were observed on surfaces exposed to 1.5 SBF. Microstructure studies revealed the widespread formation of a typical HAp structure in Si_3N_4 samples, whereas it was less prevalent in SiAlON samples. This behavior is discussed, particularly considering the grain boundary phase's influence on HAp formation tendency.

1. Introduction

Silicon nitride (Si_3N_4) ceramics have garnered significant attention, particularly in applications demanding exceptional mechanical performance characteristics such as bearings, inserts, and turbine parts. The wide adoption of Si_3N_4 can be attributed to its advantageous attributes, including low density, high elastic modulus, outstanding wear resistance, exceptional hardness, and high fracture toughness as a self-reinforced material. Furthermore, its capability to maintain these properties at elevated temperatures further extends its utility. Some of these attributes also hold substantial importance in structural biomedical applications. Moreover, Si_3N_4 exhibits noteworthy suitability for bioapplications due to its high chemical inertness towards body fluids, non-magnetic properties, and semi-permeability to X-rays—an essential feature for diagnostic imaging techniques. Additionally, Si_3N_4 boasts biocompatibility and antibacterial properties. Notably, Si_3N_4 contains biologically accepted elements, with nitrogen (N) being a natural component of the human body. Studies have indicated that the release of Si ions contributes to osteoblast formation and prevents bone destruction (osteoclast) [1]. Si_3N_4 has demonstrated non-cytotoxic behavior in previous studies [2], and its antibacterial activity surpasses that of widely used biomaterials like titanium (Ti) and polyether ether ketone (PEEK) [3].

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Nowadays, due to some limitations of alumina and zirconia bioceramics, silicon nitride has been investigated to be used in clinical applications mainly in situations where bone replacement is required [4]. They hold promise for applications in joint prostheses, mini bone stabilizers, intervertebral screws, spinal operations, and traumatology. However, for biological applications, additional properties such as bioactivity, facilitating strong bonding with body tissues, are often required. The initial study on silicon nitride biocompatibility in 1980 yielded discouraging results [5]. However, in 1989, Howllet et al. [6] demonstrated that porous silicon nitride obtained via reaction bonding favored bone growth in vivo. Notably, in 2018, a report on 30-year clinical outcomes of lumbar fusion surgeries employing silicon nitride implants marked a significant milestone [7]. This study represented the first clinical evaluation of silicon nitride as an implant material, the debut of commercial anterior lumbar interbody fusion using a synthetic material, the introduction of a spinal interbody implant design featuring endplate porosity to promote fusion, and the longest clinical follow-up for any implant material in spine surgery. To enhance bioactivity, numerous surface-altering techniques are under investigation, aiming to improve performance in biological environments while preserving the bulk properties of Si3N4. These surface studies encompass surface modification techniques [8,9] and overcoating methods such as grafting [10] or thin film deposition [11,12]. The overcoated layer is typically kept as thin as possible to bolster mechanical performance through improved bonding strength and reduced residual stresses [13]. Thicker coatings are more prone to delamination and cracking.

Calcium phosphate-based ceramics, particularly hydroxyapatite (HAp), $Ca_{10}(PO_4)_6(OH)_2$, are commonly employed as coatings for orthopedic prostheses. HAp swiftly integrates with bones and stimulates new bone growth, making it highly valuable. Nevertheless, HAp's inherent brittleness and relatively poor mechanical properties, notably its low fracture toughness, limit its use, rendering it more attractive as a thin coating material rather than for direct use in bulk form. Studies have compiled information on the thicknesses achieved through various techniques for depositing HAp coatings on metallic biomaterials, discussing coating materials, techniques, thickness, and adhesion quality [14]. Additionally, successful coating of Si_3N_4 ceramics with HAp using different methods has been reported [12,15].

Consequently, this study endeavors to compare Si_3N_4 and SiAlON substrates in terms of their potential to deposit hydroxyapatite in concentrated simulated body fluid (SBF)

2. Experimental Procedure

The Si_3N_4 substrates utilized in this investigation were procured from a commercial supplier, namely MDA Advanced Ceramics Ltd., located in Turkey. These substrates were fabricated through gas pressure sintering, incorporating densification additives, employing methods consistent with previous reports [16]. In the manufacturing process of these specimens, Si_3N_4 powder (Ube SN E-10, Ube City, Japan) was milled with sintering additives and subsequently cold-pressed at room temperature to form square-shaped samples. Then samples were sintered under nitrogen via gas pressure sintering, reaching temperatures exceeding 1700 °C. These substrates were utilized in their as-received (as-fired) state, without of any polishing step. Prior to the coating process, ultrasonic surface cleaning was executed using a sequence of acetone, 70% ethanol, and deionized water separately, each for 15 minutes. Then, the cleaned samples were exposed to sodium silicate solution (SS) at 37 °C for seven days. After the incubation period, the samples were washed in distilled and deionized water and dried at room temperature. Afterwards, the samples were immersed in SBF under controlled conditions, specifically at a temperature of 36.5 ± 0.5°C and a pH of 7.4. The SBF solution was prepared using a recipient originally developed by Kokubo et al [17]. The SBF solution was refreshed every other day to stabilize the ion concentration. At the end of seven days, the samples were washed in distilled water to remove any residual salts on the surface and dried at room temperature. The same procedure was also applied to the recipe prepared with a 1.5 times higher concentration. After drying, surfaces were observed using a scanning electron microscope (SEM) (Hitachi SU5000) equipped with a field emission gun using a secondary electron imaging mode. In addition, an energy-dispersive X-ray spectrometer (EDS) is used for elemental analysis. Samples were Pt-coated before observation. The samples were immersed in SBF under controlled conditions, specifically at a temperature of 36.5 ± 0.5°C and a pH of 7.4. The concentrated (1.5) SBF solution was prepared using a formulation adapted from the recipient originally developed by Kokubo et al [17].

3. Results and Discussion

The biomimetic coating was administered in two sequential steps: i) nucleation facilitated by a sodium silicate solution (SS), and ii) precipitation and growth of the apatite layer achieved through the use of concentrated simulated body fluid (SBF) with a concentration of 1.5 times the standard SBF. The inclusion of sodium silicate solution in the process enhances the second step (precipitation and growth). In this procedure, the initial adsorption of silicate ions from the solution takes place on the ceramic surface. Subsequently, nucleation of hydroxyapatite begins on these adsorbed ions as the samples are immersed in SBF, leading to the progressive thickening of the coating as hydroxyapatite continues to form [12]. As established in prior research, the concentration of sodium silicate employed in this process plays a critical role in promoting the formation of a hydroxyapatite layer by the conclusion of the coating process [18].

The coating underwent examination through secondary electron imaging (SI) for image analysis and Energy-Dispersive X-Ray Spectroscopy (EDS) for chemical characterization, with the outcomes presented in Figure 2 and Figure 2, respectively.

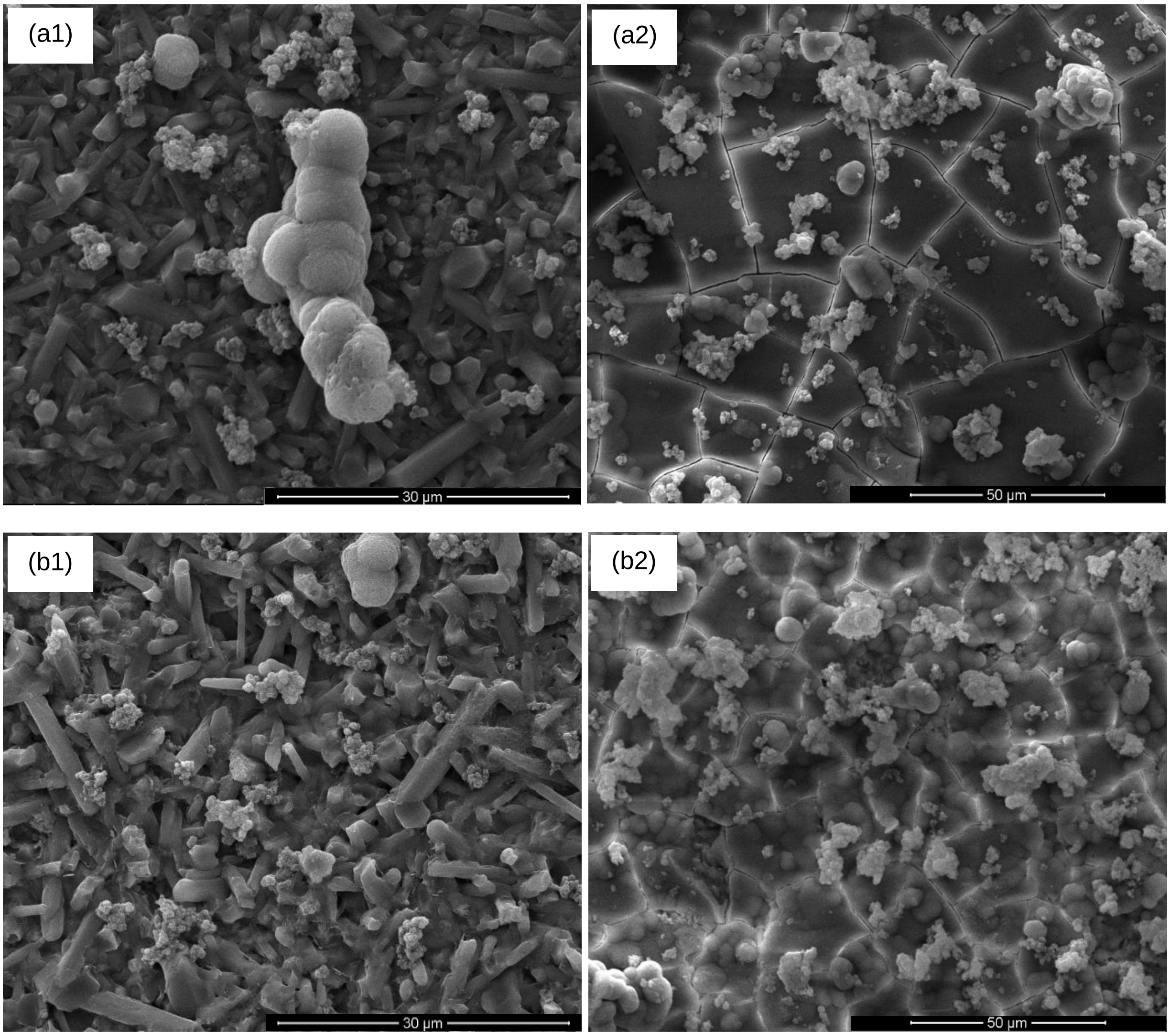
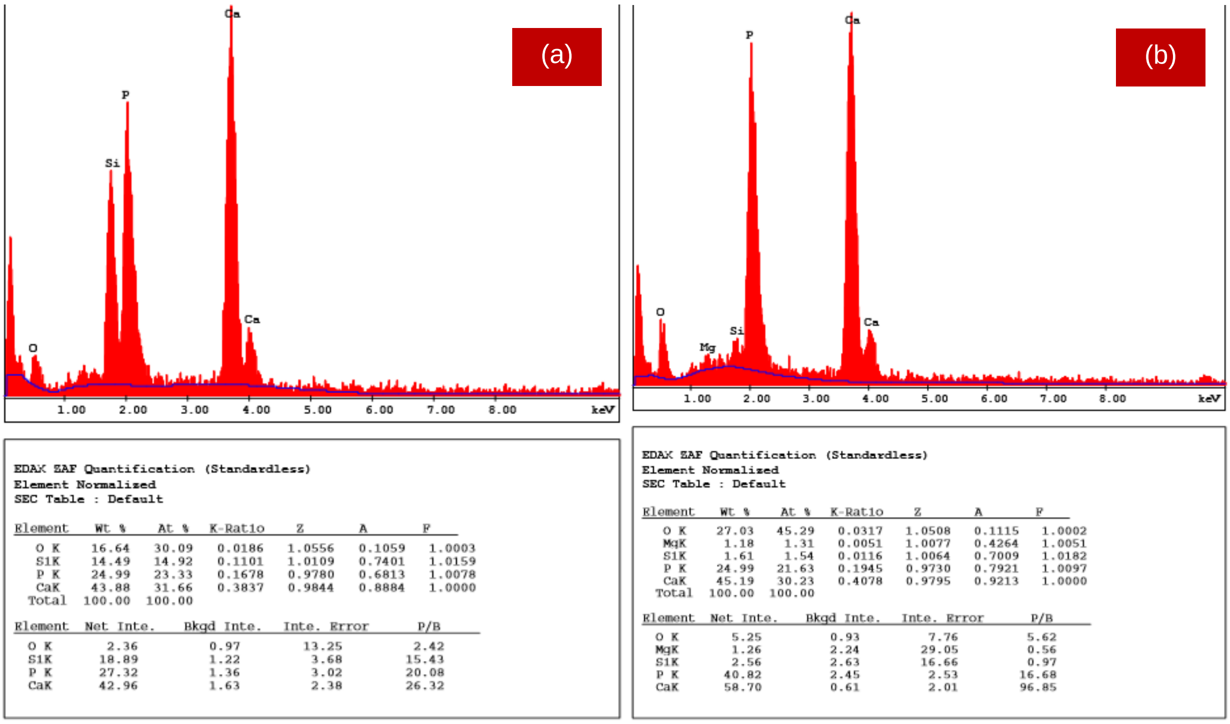


Figure 1. SI images of the coated (a) Si_3N_4 and (b) SiAlON substrates



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EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %     At %    K-Ratio     Z          A         F
  O K     16.64    30.09    0.0186    1.0556    0.1059    1.0003
  SiK     14.49    14.92    0.1101    1.0109    0.7401    1.0159
  P K     24.99    23.33    0.1678    0.9780    0.6813    1.0078
  CaK     43.88    31.66    0.3837    0.9844    0.8884    1.0000
 Total   100.00   100.00

Element  Net Inte.    Bkgd Inte.   Inte. Error      P/B
 O K         2.36         0.97         13.25          2.42
 SiK        18.89         1.22          3.68         15.43
 P K        27.32         1.36          3.02         20.08
 CaK        42.96         1.63          2.38         26.32
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EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %     At %    K-Ratio     Z          A         F
  O K     27.03    45.29    0.0317    1.0508    0.1115    1.0002
  MgK      1.18     1.31    0.0051    1.0077    0.4264    1.0051
  SiK      1.61     1.54    0.0116    1.0064    0.7009    1.0182
  P K     24.99    21.63    0.1945    0.9730    0.7921    1.0097
  CaK     45.19    30.23    0.4078    0.9795    0.9213    1.0000
 Total   100.00   100.00

Element  Net Inte.    Bkgd Inte.   Inte. Error      P/B
 O K         5.25         0.93          7.76          5.62
 MgK         1.26         2.24         29.05          0.56
 SiK         2.56         2.63         16.66          0.97
 P K        40.82         2.45          2.53         16.68
 CaK        58.70         0.61          2.01         96.85
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Figure 2. EDS results of the coated (a) Si_3N_4 and (b) SiAlON substrates

Achieving densification in both Si_3N_4 and SiAlON materials necessitates the introduction of metal oxides to create liquid phases at elevated temperatures, resulting in a liquid phase sintering process. Upon cooling, this process yields an intergranular oxynitride glassy phase with a thickness of approximately 1–1.5 nanometers. This intergranullar phase plays an important role on mechanical and high-temperature properties [19]. Within the SiAlON system, a segment of the grain boundary phase becomes incorporated into the crystal structure via the formation of a solid solution, yielding the SiAlON material. SiAlONs are solid solutions composed of Si_3N_4 and Al_2O_3, wherein aluminum and oxygen replace silicon and nitrogen, respectively. As a result, when we contrast Si_3N_4 with SiAlON, it becomes evident that Si_3N_4 possesses a significantly greater quantity of the grain boundary phase. Upon comparing these two systems, it was apparent that the characteristic formation of the HAp structure was present in both cases. However, it was more prominently distributed in the Si_3N_4 samples, while being less prevalent in the SiAlON samples. This is believed to have occurred due to the influence of oxygen-rich grain boundary phases on HAp deposition.

The apatite layer formed on silicon nitride surfaces after the immersion into 1.5 SBF revealed the existence of calcium, phosphorous, magnesium, silicon and oxygen ions (Figure 2), confirming the presence of PO_4^{3-} and CO_3^{2-} groups and leading to the formation of apatite phase. The molar Ca/P ratios that had values corresponding to non-stoichiometric biological apatite were obtained in each case (1.36 on the Si_3N_4 substrate and 1.4 on the SiAlON substrate).

4. Conclusions

Si_3N_4 and SiAlON ceramics were compared regarding their potential to deposit hydroxyapatite in simulated body fluid (SBF) with varying concentrations. It was observed that typical HAp structure formation was very widespread in Si_3N_4 samples and it was less spread in SiAlON samples. Since Si_3N_4 is more rich in terms of grain boundary oxynitride phase rather than SiAlON on the surface the result obtained in this study presents the importance of grain boundary phase amount on the tendency of HAp formation.

The apatite layer formed on silicon nitride surfaces after the immersion into 1.5 SBF was analyzed by EDX. Calcium, phosphorous, magnesium, silicon and oxygen ions were identified, confirming the presence of PO_4^{3-}

and CO_3^{2-} groups and leading the formation of apatite phase. The molar Ca/P ratios that had values corresponding to non-stoichiometric biological apatite (Ca/P molar ratio 1.67) were obtained.

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Declaration of Competing Interest

No conflict of interest was declared by the authors.

Authorship Contribution Statement

Seniz R. KUSHAN AKIN: Writing, Reviewing, Editing, Analysis & Interpretation of Results and Manuscript Preparation

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