Electrospun Chitosan/Silver Doped-Hydroxyapatite Nano-Fibers on Thermal Conductivity Modified Si$_3$N$_4$ Ceramics with Different Sintering Cooling Rate

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Abstract Dental implants are exposed to cycle loadings and thermal changes. The thermal properties of the materials in dentistry are important in terms of the biological changes that these materials will create in living tissues. The intraoral environment is very complex and demanding and thermal changes can occur. For example, the normal temperature of the oral cavity varies between 32-37°C, while eating, it can vary between 0-80°C with hot-cold foods [1-2]. The high thermal internal stresses that occur in implants exposed to temperature changes cause cracks or even fractures in the implants. Also pending the drilling of the

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1. Introduction

The thermal properties of the materials used in dentistry are important in terms of the biological changes that these materials will create in living tissues. The intraoral environment is very complex and demanding and thermal changes can occur. For example, the normal temperature of the oral cavity varies between 32-37°C, while eating, it can vary between 0-80°C with hot-cold foods [1-2]. The high thermal internal stresses that occur in implants exposed to temperature changes cause cracks or even fractures in the implants. Also pending the drilling of the
bone, the temperature could increase above 47°C and cause irreversible osteonecrosis. The result is weakened contact of implants with bone and possible loss of rigid fixation. It is important to find an optimal condition where the increase in bone temperature during the bone drilling process would be minimal [3]. Because of these considerations, new materials are needed to solve these problems.

Since Si₃N₄ is inert and biocompatible materials with low density, high fracture toughness and mechanical strength, it is suitable for use in dental implants such as implants exposed to cyclic load and is the preferred material of recent years [4-5]. Thermal shock resistance strongly affects the microstructure and mechanical and thermal properties [6]. It may be developed with elongated Si₃N₄ grains for higher thermal shock resistance [7]. The thermal expansion coefficient of Si₃N₄ is 3.0-3.5 (10⁻⁶ K⁻¹) (25-1000°C), it is the important parameter that affects the thermal shock resistance. To improve the thermal shock resistance of Si₃N₄, thermal conductivity should be increased [8-9]. The theoretical thermal conductivity of β-Si₃N₄ is 200-320W/mK at room temperature. Although it has a high theoretical thermal conductivity, commercially available conductivity values are low due to factors such as grain boundary phases and lattice defects in Si₃N₄ crystal [10-13]. However, it is not enough to investigate its thermal properties in the biomedical field [13]. MgO is known to be biodegradable oxide [14-15], SiO₂ nanoparticles are employed in the fabrication as drug-delivery systems in nanomedicine [16]. Although there are biomedical studies on yttrium oxide (Y₂O₃) nanoparticles [17], there is no current study on the effect of Y₂O₃ additives on the thermal conductivity of biomedical Si₃N₄ ceramics. High oxygen affinity sintering additives as Y₂O₃ should be used to reduce the defects in Si₃N₄. Also, the effect of the cooling properties during sintering on the MgO, SiO₂ and Y₂O₃ included Si₃N₄ substrates was purposed as wt. 3%, 7% and 3% in Si₃N₄ compositions, respectively. After mixing according to the given proportions of all the powders and milling in a planetary mill (at 300 rpm, for 90 min. in isopropyl alcohol) (Fritsch-Pulverisette 5, Germany); the slurries were dried with a rotary evaporator (Heidolph 4001, Germany). The sintering process was performed via the gas pressure sintering furnace (GPS) (KCE-FPW 100/150-2200-25) at 1775°C for 2 hours under 5 bar nitrogen gas pressure with two different cooling rates as fast and slow cooling. Silver doped hydroxyapatite (HAPs) and CTs (medium molecular weight) powder (<100 nm in particle size) were purchased from Nanotech Co. in Turkey.

The bulk density of the sintered samples was measured using the Archimedes methods (according to the standard ASTM-C373). The phase analyses of the samples were by X-ray diffraction method (XRD, Rigaku Rint 2000, Japan) equipped with Cu-Kα (λ = 1.54056 Å) radiation (scanning speed: 1°C/min.). Morphological investigations were performed using scanning electron microscopy (SEM, Zeiss SUPRA 40 VP-FEG, Germany). Thermal diffusivity measurements using a laser-flash device (Netzsch LFA-457, Germany). A heat capacity (Cp) of 0.71J/g-K was used for all the samples [23]. The Vickers hardness of the polished sample was measured by the HV-1000B micro Vickers tester under 1000 g load with a dwell time of 20 s. The compressive strength of the composites was estimated by the Mares Test-10 tons test unit. The electrospinning of the CTs/HAPs (wt. 1% HAPs in CTs) fiber coating on Si₃N₄ substrate was performed. Electrospinning was performed under environmental conditions. The electrospinning voltage, nozzle to substrate distance and solution flow rate were optimized as 16 kV, 10 cm and 0.03ml/min, respectively.

3. Result and Discussions

Figure 1 (a-d) gives the characterization of the starting powders. The particle size distribution of Si₃N₄ and HAPs powder are under the 1 µm and 100nm which confirm

2. Materials and Methods

The MgO (purity 99.9%, Sigma Aldrich, USA), Y₂O₃ (purity 99.9%, Sigma-Aldrich, USA) and SiO₂ (purity 99.9%, Sigma Aldrich, USA) additives and α-Si₃N₄ (<1 µm UBE Industries Co., Japan) starting powder were used for the formation of a highly dense structure with high thermal conductivity. The ratio of MgO, Y₂O₃ and SiO₂ was selected as wt. 3%, 7% and 3% in Si₃N₄ compositions, respectively. After mixing according to the given proportions of all the powders and milling in a planetary mill (at 300 rpm, for 90 min. in isopropyl alcohol) (Fritsch-Pulverisette 5, Germany); the slurries were dried with a rotary evaporator (Heidolph 4001, Germany). The sintering process was performed via the gas pressure sintering furnace (GPS) (KCE-FPW 100/150-2200-25) at 1775°C for 2 hours under 5 bar nitrogen gas pressure with two different cooling rates as fast and slow cooling. Silver doped hydroxyapatite (HAPs) and CTs (medium molecular weight) powder (<100 nm in particle size) were purchased from Nanotech Co. in Turkey.
with the SEM image. Figure 2 (a-b) gives the GPS sintered Si₃N₄ substrate for the fast (70°C/min from 1775 °C to RT) and slow cooling process. The slow cooling process was applied in three stages: 10°C/min from 1775 to 1700°C, 5°C/min from 1700 to 1400°C, and 70°C/min form 1400°C to RT. It gives that both fast and slow cooled Si₃N₄ samples have porosity. The porosity and its size for fast cooled samples are less than the slowly cooled samples.

Figure 1. Particle size (a-b) and SEM images (c-d) of the starting powder: a-c) Si₃N₄, b-d) HAPs
The density, mechanical and thermal properties of the fast and slow cooled Si$_3$N$_4$ composites are listed in Table 1 and given in Figure 3. Although there is no significant change in density and thermal conductivity depending on the cooling rate, there is a very serious change in the mechanical properties in fast cooling. The thermal conductivity of the fast and slow cooled samples depending on the temperature was detected in Figure 3. Thermal conductivity was measured at room temperature, 40°C, 55°C, 70°C and 85°C, for fast cooled samples, 46.35, 44.50, 42.12, 40.24 and 38.22 W/mK, respectively. The thermal conductivity for the slowly cooled samples was obtained as 44.60, 42.81, 40.42, 38.51 and 36.58 W/mK, respectively. As the measurement temperature increases, since the high frequency and low wavelength phonons are more effective in the transport of heat energy, the thermal conductivity decreases due to the Umklapp process, which reduces the average free path of the phonons, and as a result of errors in the structure, the number of scattering increases [24-27]. The fast cooled samples are higher than the slowly cooled samples for all temperatures. The reduction of mechanical and thermal properties for slowly cooled samples can be explained that the grain growth mechanisms along with the length and width directions that occur for the grain growth of β-Si$_3$N$_4$ under nitrogen pressure. The grain growth of Si$_3$N$_4$ is related to the formation is the viscosity of the liquid phase formed during sintering, which depends on the sintering additives as metal oxides and cooling rate. The Ostwald ripening mechanisms which diffusion process has a critical role on the grain growth in Si$_3$N$_4$ materials. The higher viscosity suppresses the nucleation and atomic transportation due to diffusion during solution precipitation. It led to promote the grain growth of Si$_3$N$_4$ [28, 29].

The high hardness and compressive strength of Si$_3$N$_4$ allow these ceramics to be used especially in load-bearing applications, but its integration with bone in the body is difficult due to the strong covalent bond structure of Si$_3$N$_4$. Also, to increase the bioactivity of implant materials and to establish a chemical bond with bone tissues, the bone that is integrated with the implant materials should have a similar structure [30]. For this reason, a functional surface coating must be essential to increase the integration speed of the Si$_3$N$_4$ samples. The fact that the polymer-based CTs in the coating structure is biodegradable and the ceramic-based HaP has the same structure as the bone will improve the interaction with the bone. Also, the hybrid coating on the base surface being in the form of fiber and having a porous structure will improve the interaction of
the implant material with body fluids since it will increase the surface area. As a result, the superior mechanical properties of the Si$_3$N$_4$ ceramic material compared to the bone, the biodegradability and bone resemblance of the hybrid CTs/HAPs can be preferred for dental and orthopedic applications. Because of these considerations, the surface of the fast cooled Si$_3$N$_4$ substrate was coated with electrospinning of CTs/HAPs. Figure 4 (a-d) gives the SEM image and EDX analyses of the electrospun CTs/HAPs. SEM images the structure and distribution of electrospun nanofibers are very porous and homogeneous. As shown in these figures, the fiber diameter is under 200nm and HAPs are embedded in CTs matrix. As given EDX analyses Ca, P, O and Ag come from the silver doped HAP, Ca/P ratio is nearly 1.67 which is very close to hydroxyapatite stoichiometry.

![SEM and EDX analyses of electrospun CTs/HAPs fibers on the Si$_3$N$_4$ substrate](image-url)

**Figure 4.** SEM and EDX analyses of electrospun CTs/HAPs fibers on the Si$_3$N$_4$ substrate
4. Conclusions

The Si$_3$N$_4$ substrates containing MgO, SiO$_2$ and Y$_2$O$_3$ for the dental purpose were successively fabricated and sintered with GPS. The effect of the cooling rate on the density, mechanical and thermal properties was observed. Also, the CTs/HAPs fibers were coated with electrospinning on the fast cooled samples. The results can be summarized as given below:

- The greater density (3.25 g/cm$^3$) and thermal conductivity (46.35 W/mK at RT) for fast cooled Si$_3$N$_4$ were observed compared with slow cooled Si$_3$N$_4$ (3.22 g/cm$^3$ and 44.60 W/mK at RT).
- The higher hardness and strength of the fast cooled substrate were measured as 1250 HV and 1800 MPa compared with slowly cooled samples (1190 HV, 1670 MPa).
- Nano HAP/CTs fibers are homogeneously deposited in porous structures with electrospinning on the surface of the fast cooled Si$_3$N$_4$ substrate to develop the surface functionality.
- This surface-functionalized Si$_3$N$_4$ ceramics can be a candidate in the field of dental applications.

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