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Production and Characterization of ZrO_2-Si_3N_4 Ceramics

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Anahtar Kelimeler

ZrO_2
Si_3N_4
Düşük sinterleme sıcaklığı
Sertlik
Tokluk

Graphical/Tabular Abstract (Grafik Özet)

In this study, ZrO_2-Si_3N_4 ceramics were brought together to use the strengths of both materials. Optimum density and mechanical property values were achieved with the addition of 5% Si_3N_4. Due to the low sintering temperature, β-Si_3N_4 was not transformed. /Bu çalışmada ZrO_2-Si_3N_4 seramikleri her iki malzemenin güçlü yönlerini ön plana çıkaracak şekilde bir araya getirilmiştir. En uygun yoğunlaşma ve mekanik özellik değerlerine %5 Si_3N_4 ilavesi ile ulaşılmıştır. Düşük sinterleme sıcaklığı nedeniyle β-Si_3N_4 gözlemlenmemiştir.

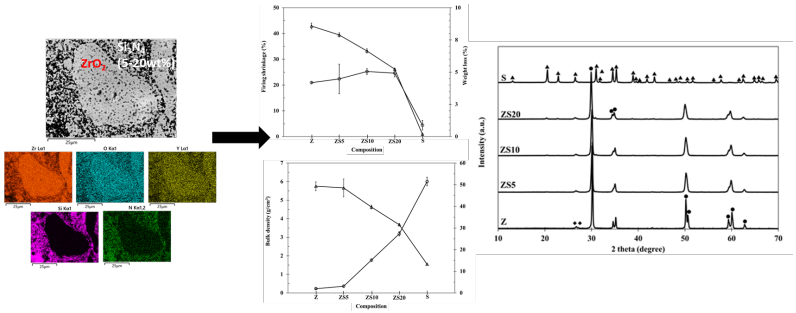


***Figure A**: Distribution of ceramic phases via EDS mapping, properties and XRD analyses /**Şekil A:** Seramik fazların EDS haritalama ile dağılımı, özellikler ve XRD analizleri*

Highlights (Önemli noktalar)

- *ZrO_2-Si_3N_4 ceramics were produced 1500°C under a nitrogen atmosphere. /ZrO_2-Si_3N_4 seramikleri 1500°C'de azot atmosferi altında üretilmiştir.*
- *The density values decreased from 5.66 to 3.68 g/cm^3 /Yoğunluk değerleri 5,66'dan 3,68 g/cm^3'e düşmüştür.*
- *The major phase found in all samples was t-ZrO_2, Si_3N_4 was detected. /Tüm numunelerde başlıca faz t-ZrO_2 (tetragonal zirkonya) olarak tespit edilmiştir.*

***Aim (Amaç):** This study aims to produce ZrO_2-Si_3N_4 ceramics with varying Si_3N_4 amounts. The effect of Si_3N_4 amount on the phase-microstructural development, hardness and fracture toughness were investigated. /Bu çalışmada, farklı oranlarda Si_3N_4 kullanılarak ZrO_2-Si_3N_4 seramiklerinin üretilmesi amaçlanmıştır. Si_3N_4 oranının faz-mikroyapı gelişimi, sertlik ve kırılma tokluğu üzerindeki etkisi incelenmiştir.*

***Originality (Özgünlük):** ZrN formation is undesirable in the production of ZrO_2-Si_3N_4 ceramics due to their mechanical properties. In order to prevent the formation of this phase, sintering was performed at a relatively low level. /ZrO_2-Si_3N_4 seramiklerinin üretiminde ZrN oluşumu malzemenin mekanik özelliklerini zayıflatmasından dolayı istenemektedir. Çalışmada fazın oluşumunu engellemek amacıyla sinterleme görece düşük sıcaklıkta yapılmıştır.*

***Results (Bulgular):** The density values decreased from 5.66 to 3.68 g/cm^3, the hardness values of samples reduced from 11.7 to 2.6 GPa by the entity of Si_3N_4 content from 5 to 20 wt. /Yoğunluk değerleri, %5 ve %20 Si_3N_4 içeren numunelerde sırasıyla 5,66'dan 3,68 g/cm^3'e, sertlik değerleri ise 11,7'den 2,6 GPa değişmiştir.*

***Conclusion (Sonuç):** Si_3N_4 addition restricted consolidation and open porosity increased from 3 to 27 for 5 and 20 wt.% of Si_3N_4 addition. XRD results indicated that ZrO_2 was detected as the major phase. Due to the low sintering temperature, α→β-Si_3N_4 phase transformation could not be observed. Both hardness and fracture toughness of the samples diminished with Si_3N_4 addition. /Si_3N_4 ilavesi yoğunlaşmayı kısıtlamış ve açık gözeneklilik, %5 ve %20 ağırlık oranlarında Si_3N_4 ilavesi için %3'ten %27'ye yükselmiştir. XRD sonuçları, ZrO_2'nin ana faz olarak tespit edildiğini göstermiştir. Düşük sinterleme sıcaklığı nedeniyle α→β-Si_3N_4 faz dönüşümü gözlenememiştir. Numunelerin hem sertliği hem de kırılma tokluğu, Si_3N_4 ilavesiyle azalmıştır.*

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Abstract

Yttria stabilized tetragonal zirconia polycrystal (Y-TZP) has been used in dental applications because of its superior mechanical properties, aesthetically pleasing appearance, low tendency to plaque accumulation and excellent biocompatibility. However, there are some drawbacks of zirconia which are related to low temperature degradation and its radiopaque property. In this study, to overcome these drawbacks by combining of beneficial properties of silicon nitride that is its antibacterial behavior, partial radiolucency, stability in aqueous environment and those of zirconia which are superior mechanical properties and translucency in visible region were studied. ZrO_2-Si_3N_4 ceramics (Si_3N_4 content varies between 0-20 wt.%.) were produced 1500°C under a nitrogen atmosphere. As the amount of Si_3N_4 in ZrO_2 was increased, densification was inhibited and the bulk density decreased gradually. The density values decreased from 5.66 to 3.68 g/cm^3 for the samples containing 5 and 20 wt.% Si_3N_4. Phase content of samples was determined by X-ray diffraction (XRD) technique. The major phase found in all samples was t-ZrO_2, Si_3N_4 was detected in α-form due to low sintering temperature. Peak merging in specific 2θ values in ZrO_2 shows the presence of c-ZrO_2. Microstructure of samples was analyzed by scanning electron microscopy (SEM). The porosity formed with Si_3N_4 addition was also determined by SEM. Hardness and fracture toughness values of samples were characterized by Vickers hardness test. Hardness and fracture toughness also decreased against the increasing amount of Si_3N_4.

ZrO_2-Si_3N_4 Seramiklerinin Üretimi ve Karakterizasyonu

Makale Bilgisi

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Öz

İtriya stabilize tetragonal zirkonya polikristali (Y-TZP); üstün mekanik özellikleri, estetik açıdan hoş görünümü, plak birikimine düşük eğilimi ve mükemmel biyouyumluluğu nedeniyle diş ile ilgili uygulamalarda kullanılmaktadır. Fakat zirkonyanın, diş ile ilgili uygulamalarda düşük sıcaklık bozunumu ve radyoopak özelliği ile ilgili bazı dezavantajları vardır. Bu çalışmada, silisyum nitrürün (Si_3N_4) faydalı özellikleri olan antibakteriyel davranışı, radyo dalgalarına karşı kısmi geçirgenlik, sulu ortamdaki kararlılığı ile zirkonyanın faydalı özellikleri olan üstün mekanik özellikleri ve görünür bölgedeki yarı saydamlığını birleştirerek bu dezavantajların üstesinden gelmek için çalışılmıştır. ZrO_2-Si_3N_4 seramikleri (Si_3N_4 içeriği ağırlıkça %0-20 aralığında değişmektedir.) 1500°C'de azot atmosferi altında üretilmiştir. Si_3N_4 miktarının artması yoğunlaşmayı engellemiş ve yığınsal yoğunluk aşamalı olarak azalmıştır. Yoğunluk değerleri, %5 ve %20 Si_3N_4 içeren numunelerde sırasıyla 5,66'dan 3,68 g/cm^3'e düşmüştür. X-ışınları kırınım (XRD) yöntemi ile numunelerin faz içerikleri belirlenmiştir. Tüm numunelerde başlıca faz t-ZrO_2 (tetragonal zirkonya) olarak belirlenmiş, düşük sinterleme sıcaklığı nedeniyle Si_3N_4 ise α formunda tespit edilmiştir. ZrO_2'de belirli 2θ değerlerinde görülen pik birleşmeleri, c-ZrO_2 (kübik zirkonya) varlığına işaret etmektedir. Numunelerin iç yapısı ise taramalı elektron mikroskobu (SEM) ile incelenmiştir. Si_3N_4 ilavesiyle oluşan gözeneklilik SEM ile de gösterilmiştir. Sertlik ve kırılma tokluğu ise Vickers sertlik testi ile karakterize edilmiştir. Si_3N_4 miktarındaki artışa bağlı olarak sertlik ve kırılma tokluğunda düşüş görülmüştür.

1. INTRODUCTION (GİRİŞ)

Transformation toughening mechanism was gained to partially stabilized ZrO_2 (PSZ) new perception of usage areas specifically in biomedical applications [1-4]. 3 mol% yttria partially stabilized tetragonal ZrO_2 (3-YSZ) is the commercial form of ZrO_2 'n dental area [5]. ZrO_2 ceramics provided the all needs

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for crowns, bridges, fixed-all dental restorations and implants thanks to the low radioactivity, optical appearance, biocompatibility, improved mechanical properties. One of the most significant advantages of ZrO_2 ceramics for biomedical applications is its superior biocompatibility. ZrO_2 ceramics are chemically inert, do not show local or systemic adverse reactions [5,6], allow good cell adhesion [5-7]. In addition, peri-implant soft tissues around ZrO_2 repaired itself faster than titanium [8]. ZrO_2 ceramics show translucency, tooth-colored shade, they are advantages for dental applications [9]. Although transformation toughening mechanism improves the mechanical resistance of ZrO_2, it restrains the usage of ZrO_2 through low-temperature degradation known as aging [5]. After prolonged exposure to water vapor at a temperature range of 100-500°C or body fluids at 37°C, progressive, spontaneous tetragonal to monoclinic phase transformation occurs with 4% volume increment. Reduction in strength, toughness, density and increase of monoclinic phase content are the detrimental effects of aging [6]. This may result in inflammatory responses [5, 7].

Si_3N_4 ceramics have been developed for structural applications as a result of high thermal, mechanical and chemical properties, by 21st century, their use in medical applications was discovered [10]. The mechanical strength of Si_3N_4 is significant in medical applications. Dense ones have been mainly investigated as load-bearing orthopedic applications for joints such as the knee, hip and spinal fusion implants. Additionally, porous form of Si_3N_4 has been studied in bone replacements. The first usage of Si_3N_4 ceramics as spinal fusion devices was begun in 1986. The use of Si_3N_4 as spinal vertebral body replacement device was started in 2006 and Si_3N_4 spinal fusion cages have been introduced since 2008 [11-13]. Non-cytotoxicity and biocompatibility properties of Si_3N_4 confirmed both in vitro and in vivo studies. In addition to non-toxicity, it improves cell adhesion, proliferation and differentiation [14-15]. Furthermore, wear particles of Si_3N_4 are soluble body fluids, it provides cell proliferation and does not cause infection [16-18]. Bacterial lysis is occurring as a result of the its surface chemistry and play an important function as a candidate material in dental applications [15,18]. When β-Si_3N_4 is implanted into an aqueous solution, ammonium ions (NH_4^+) are produced and show a pH-buffering effect [10-19]. The surrounding acidic gel is transformed to the alkaline values because of this effect. These alkaline values prevent adhesion and biofilm generation of bacteria. Furthermore, it has low wetting angle and high hydrophilicity with a negative charge. When same charge

d bacteria meet Si_3N_4, membrane is degraded and cell of bacteria is died [18]. Si_3N_4 is a radiolucent material visible on plain radiographic images [15]. Si_3N_4 provides significant benefit; it does not distort images and serves exact imaging of the implant during the surgical process owing to the radiolucency. According to the researchers, the radiographic behavior is the same as enamel and does not show artifacts, thus distinguishing surrounding tissue [20]. The chemical stability of Si_3N_4 was proved when exposed to accelerated aging due to research that preserved its superior flexural strength and its usage in vivo [18].

To improve the properties of ZrO_2 in dental applications, Si_3N_4 can be preferred as a secondary phase in ZrO_2. High toughness, chemical stability in aqueous environment resistance, radiographic response and antibacterial behavior of Si_3N_4 can be combined with high fracture toughness, optical translucency and radioopacity of ZrO_2. A comparison of the remarkable properties of ZrO_2 and Si_3N_4 ceramics is listed in Figure 1.

ZrO_2	Property	Si_3N_4
Improved (transformation toughening)	Toughness	Improved (microstructural toughening)
High (similar to tooth)	Optical translucency	No
High (similar to Titanium)	Radioopacity	No
No	Radiolucency	High
Bioinert (Non-toxic)	Biocompatibility	Bioinert (improves proliferation)
No	Antibacterial	High (pH buffering, (-) charge)
High (transformation toughening)	Aging	No

Figure 1. A comparison of the remarkable properties of ZrO_2 and Si_3N_4 ceramics (ZrO_2 and Si_3N_4 seramiklerinin önemli özelliklerinin karşılaştırılması)

This study aims to produce ZrO_2-Si_3N_4 ceramics with varying Si_3N_4 amounts at a moderate temperature to prevent formation of ZrN. The effect of Si_3N_4 amount on the phase-microstructural development, hardness and fracture toughness were investigated.

2. MATERIALS AND METHODS (MATERYAL VE METOD)

2.1. Sample Preparation (Numune Hazırlama)

Si_3N_4 powder (UBE SN-E10, Japan.) and ZrO_2 powder (Inframat Advanced Materials, USA) were preferred as the starting powders. Their properties are given in Table 1.

Table 1. General properties of starting raw materials (Başlangıç hammaddelerin özellikleri)

RAW MATERIALS	VALUE
Si_3N_4 powder	
α phase	> 95 wt.%
Oxygen Content	<2 wt.%
Specific Surface Area	9-13 m^2g^{-1}
ZrO_2 powder	
Purity	≥ 99.9 wt.%
Yttria Stabilized ZrO_2(YSZ)	3 mol %

3.46 wt.% Y_2O_3 (Grade C, H.C. Starck, Germany) and 3.46 wt.% CeO_2 (Inframat, USA) were used as sintering agents. Three compositions were prepared with the addition of 5, 10 and 20 wt.% of Si_3N_4 into ZrO_2 powder. The sample labels and their compositions are given in Table 2.

Table 2. Composition labels and contents (Kompozisyon isimlendirmesi ve içerikleri)

SAMPLE LABELS	CONTENTS
Z	ZrO_2 + 6.16 wt.% Y_2O_3
S	Si_3N_4 + 3.46 wt.% Y_2O_3 + 3.46 wt.% CeO_2
ZS5	95 wt.% Z + 5 wt.% S
ZS10	90 wt.% Z + 10 wt.% S
ZS20	80 wt.% Z + 20 wt.% S

Wet-milling of Si_3N_4 containing mixtures was done in a 500 cm^3 polypropylene jar with Si_3N_4 balls and a ball-to-slurry ratio was selected as 4:6. Separately, Z powder was produced by using ZrO_2 balls. Slurry was milled at 185 rpm in ethanol for 24 hours. The homogenized forms were dried in a drier at 110°C for 1 day. The produced powders were ground and sieved. Uniaxial dry press (MSE Technology) was used for forming. Powder mixtures were compacted as disk shape (radius: 10 mm, thickness: 1 mm) at 25°C and under 50 MPa.

Samples were sintered in a tube furnace (GSL-1700X, MTI Corporation, USA) under a nitrogen atmosphere at 1500°C with a hold time of 60 minutes. The heating and cooling rates were 5°C per minute to stabilize the tetragonal phase at room temperature.

2.2. Characterization (Karakterizasyon)

The density measurement was provided by Archimedes' displacement method. Phase identification was characterized by X-ray diffraction (XRD) (Rigaku MiniFlex) analysis by using Cu Kα radiation at 40 kV and 15 mA, X-ray scanning range from 10 to 70 degrees. Polished surfaces of samples were characterized by scanning electron microscopy (SEM) (Hitachi SU5000, Japan) with an energy dispersive spectrometer (EDX) (Oxford X-MaxN 80). Vickers hardness testing method determined the samples' hardness (Shimadzu HMV-G, Japan) under a load of 10 N for 10 s. Five indents were taken from each sample. The fracture toughness was identified by the measurement of the diagonal crack length from the Vickers hardness indent [21].

3. RESULTS AND DISCUSSION (BULGULAR VE TARTIŞMA)

3.1. Densification of ZrO_2-Si_3N_4 Ceramics (ZrO_2-Si_3N_4 Seramiklerinin Yoğunlaşması)

Fig. 2. gives the shrinkage and weight loss of samples. The highest shrinkage reached in Z by 42.91% showing a higher consolidation rate. A gradual decrease in shrinkage was obtained with an increasing amount of Si_3N_4. The lowest value reached was 0.95% for sample S. The weight losses of ZrO_2-containing samples were around 4% due to binder content in the initial ZrO_2 powder.

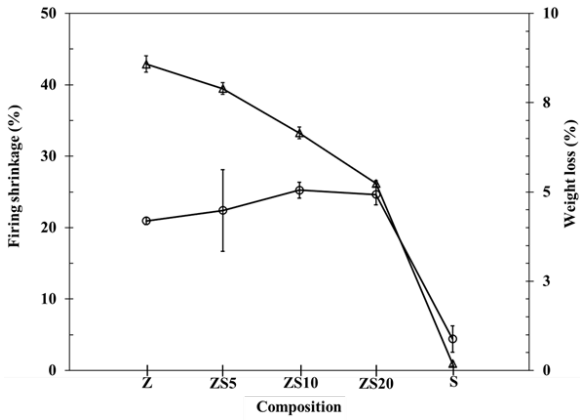


Figure 2. Firing shrinkage and weight loss values of samples (Δ: firing shrinkage, O: weight loss) (Pişme küçülmesi ve ağırlık kaybı değerleri ((Δ: pişme küçülmesi, O: ağırlık kaybı))

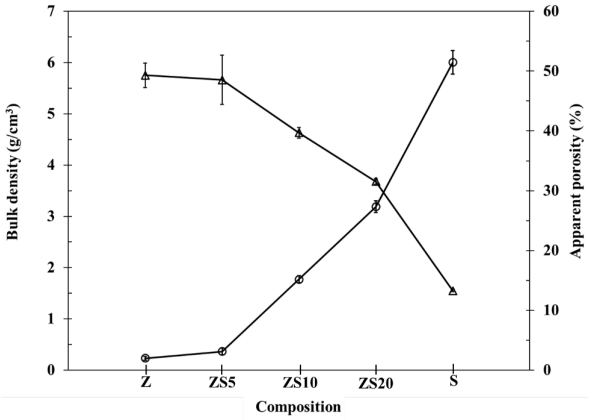


Figure 3. Bulk density and apparent porosity of samples (Δ: bulk density, O: apparent porosity) (Numuneleri yığınsal yoğunluk ve açık gözenek değerleri (Δ: yığınsal yoğunluk, O: açık gözenek)

Bulk density and apparent porosity vary with the Si_3N_4 addition. The highest bulk density was obtained for sample Z according to Figure 3. Amat et al. reached fully consolidated ZrO_2 between 1400-1600°C by using the same powder source [22]. Y_2O_3 is one of the well-known agents that stabilizes metastable tetragonal ZrO_2 phase at room temperature and hence provides transformation toughening. Ewais et al. showed the function of Y_2O_3 and CeO_2 during the sintering of Si_3N_4-ZrO_2 composites. Both oxides decrease or eliminate the risk of formation of ZrN or ZrO_xN_y phases through nitridation of ZrO_2 [23]. Moreover, CeO_2 reduces the liquidus temperature in sintering and improves densification at lower temperatures [24]. Therefore, Y_2O_3 and CeO_2 were selected as sintering additives. Despite using these additives, density started to decline against the increasing amount of Si_3N_4 and a rapid decrease was observed from ZS5 to ZS10 with values of 5.66 to 4.63 g/cm^3. The lowest densification (1.55 g/cm^3 bulk density with 51.55 apparent porosity) was reached for sample S owing to the low sintering temperature. ZrO_2 could be reduced to ZrN by a reaction with Si_3N_4 at high temperatures and under reducing atmospheres. To eliminate the risk of ZrN formation, sintering was carried out at a relatively lower temperature [25].

3.2. Phase Analysis of ZrO_2-Si_3N_4 Ceramics (ZrO_2-Si_3N_4 seramiklerinin faz analizleri)

XRD patterns of all samples are given in Fig. 4. Sample Z was composed of t-ZrO_2 (PDF Card #: 00-050-1089) and two peaks at 20 and 26.8° were matched with the two most intense peaks of zircon (PDF Card #:01-072-0402). In sample S, α-Si_3N_4 (PDF Card #: 01-070-3756) phase was observed. It was clear that a majority of α-Si_3N_4 was retained without transformation into β-Si_3N_4 which can be related to the insufficient sintering temperature. Sintering additives of Si_3N_4 that is Y_2O_3 and CeO_2 peaks were not detected in the XRD pattern. This is because of the reaction of a part of Si_3N_4 with Y_2O_3 and CeO_2 forming a liquid phase at the sintering temperature.

In ZS5, peaks of t-ZrO_2 and traces of α-Si_3N_4 were detected. The intensity of adjacent peaks at 34-35°, 50-51° and 59-60° was decreased and they merged into a single peak showing the mix of tetragonal and cubic phases. ZS10 had a slightly higher amount of Si_3N_4 than the ZS5 sample. Peak merging at 34-35° disappeared; they were observed as distinct peaks due to the presence of α-Si_3N_4 peaks at 34-35°. The entity of Si_3N_4 peaks is more evident in ZS20. Although this sample has the highest Si_3N_4 content, the peak intensity is still weak. Chockalingam and Amarakoon produced Si_3N_4-ZrO_2 composites with varying amounts (10-40 wt.%) of ZrO_2 additions. They also found that the peak intensities of ZrO_2 became higher after 25 wt.% addition [25]. In another study, TiO_2-coated Si_3N_4-ZrO_2 composites (80 wt.% Si_3N_4-20 wt.% ZrO_2) was produced. Even though the amount of ZrO_2 added is low, the most intense peak in XRD belongs to this phase [26].

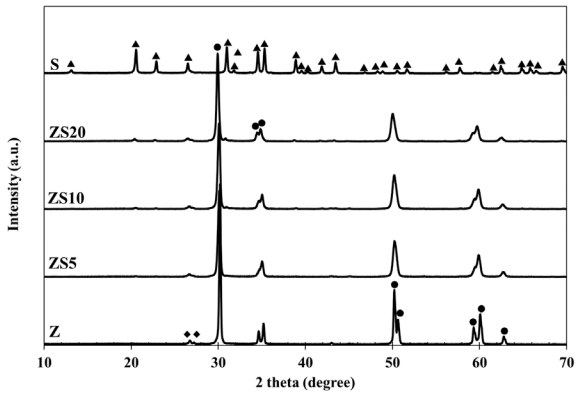


Figure 4. XRD patterns of samples (●:t- ZrO_2, ▲:α-Si_3N_4, ◆: Zircon) (Numunelerin XRD analizleri ((●:t- ZrO_2, ▲:α-Si_3N_4, ◆: Zirkon)

3.3 Microstructural Analysis of ZrO_2-Si_3N_4 Ceramics (ZrO_2-Si_3N_4 seramiklerinin iç yapı analizi)

Fig. 5 a-c shows the effect of the amount of Si_3N_4 on the microstructure. The phase distribution of ZrO_2 and Si_3N_4 can be identified easily. Due to the higher atomic weight of ZrO_2, light gray areas represent this phase, dark gray regions belong to Si_3N_4 and black areas represent porosity. At low content of Si_3N_4 (ZS5), the volume of pores is less and they are isolated. The amount of porosity gradually increased with the increase in Si_3N_4. Also, they become interconnected with each other. Low sintering temperature and low amount of sintering additives that form an insufficient liquid phase are the main causes of incomplete densification. Specific equipment such as hot press, hot isostatic press and microwave sintering have been used in the production of Si_3N_4-ZrO_2 ceramics. These ceramics reached 99% theoretical density. Sanders and Mieskowski sintered Si_3N_4-ZrO_2 ceramics at 2140°C under 2.5 MPa N_2 pressure for 0.5 h. The highest relative density obtained was 99.2% [27]. Kleebe et al. used 10 MPa pressure and 1925°C temperature and ceramics had theoretical density values varying between 98.0% and 99.6% [28]. Microwave sintering was applied using 2.45 GHz microwave energy at 1600°C for 1 h by Chockalingam and Amarakoon. 99% of theoretical density was concluded but ZrN was formed for all samples [25].

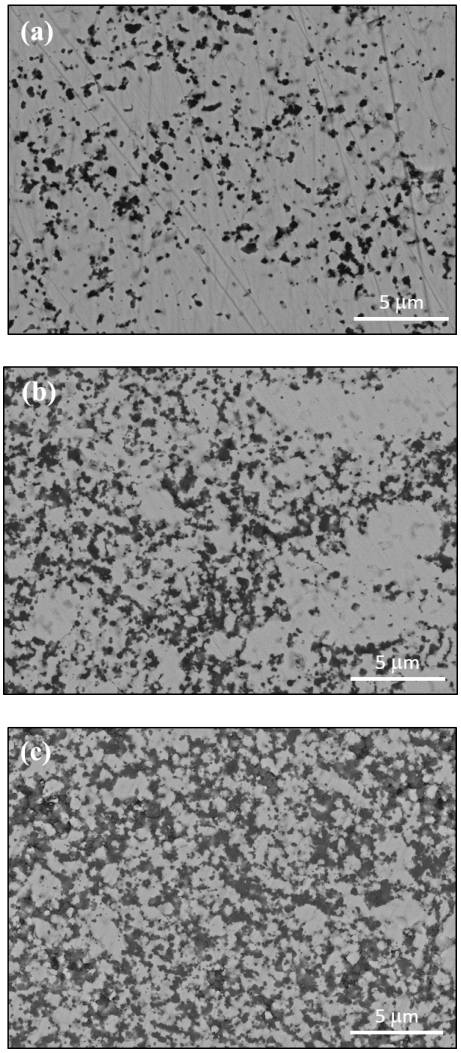


Figure 5. Microstructures of samples a) ZS5, b) ZS10 and c) ZS20 (a) ZS5, b) ZS10 and c) ZS20 numunelerine ait iç yapıları

Chemical analysis of sample ZS10 was carried out via SEM-EDX mapping as given in Fig. 6. The elemental distributions are presented in the figure. The presence of ZrO_2 in bright areas with Y can be seen. Si and N elements were detected in dark gray areas proving the presence of Si_3N_4.

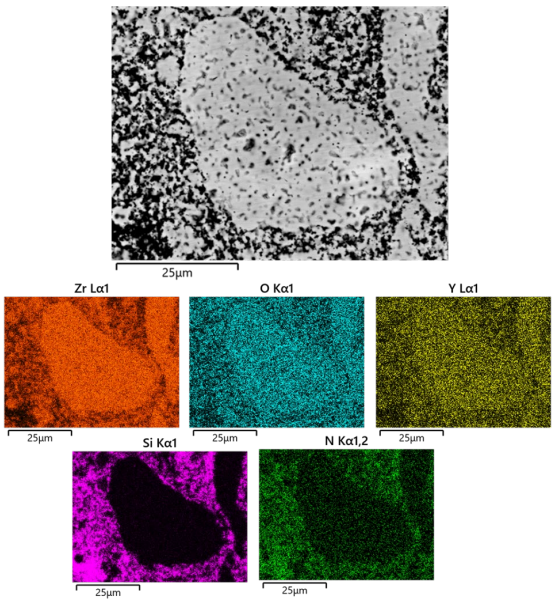


Figure 6. EDX-Mapping of ZS-10 sample (ZS-10'a air EDX-haritalama)

3.3 Hardness and Fracture Toughness of Samples (Numunelerin Sertlik ve Kırılma Tokluğu)

In Table 3 Vickers hardness and fracture toughness of Z, ZS5, ZS10 and ZS20 are shown. Porosity present in S sample have made it impossible to measure hardness value. The hardness values of samples reduced from 11.7 to 2.6 GPa by the entity of Si_3N_4 content from 5 to 20 wt.%. Traditional Si_3N_4 ceramics have 17-20 GPa hardness values, therefore an enhancement in hardness values was anticipated against the rise in Si_3N_4 content. However, full densification could not be reached due to an insufficient amount of liquid phase in Si_3N_4 samples and sintering temperature, lower hardness values were obtained. The Vickers hardness value of YSZ is 11-13 GPa [29]. On the other side, the results of the Z sample were as expected at 13.2 GPa. Fracture toughness of Z and ZS5 could be measured, owing to the high porosity content of the remaining samples, crack length after the indentation cannot be identified. Fracture toughness of Z and ZS5 measured 5.8 and 3.5 $MPa/m^{1/2}$, respectively. Mao et al. improved the fracture toughness of porous Si_3N_4 from 4.2 to 5.7 $MPa/m^{1/2}$ with the addition of 10 wt.% of ZrO_2 [30].

Table 3. Hardness and fracture toughness values of samples (Numunelerin sertlik ve kırılma tokluğu değerleri)

Sample	Hardness (GPa)	Fracture Toughness ($MPa/m^{1/2}$)
Z	13.2 (± 0.5)	5.8 (± 0.2)
ZS5	11.7 (± 0.8)	3.5 (± 0.3)
ZS10	6.1 (± 0.2)	Not measured
ZS20	2.6 (±0.2)	Not measured
S	Not measured	Not measured

4. CONCLUSIONS (SONUÇLAR)

ZrO_2 ceramics with 5-20 wt.% Si_3N_4 addition have been produced in this study. To prevent ZrN formation, samples were sintered at 1500°C under nitrogen atmosphere. Si_3N_4 addition restricted consolidation and open porosity increased from 3 to 27 for 5 and 20 wt.% of Si_3N_4 addition. XRD results indicated that ZrO_2 was detected as the major phase. Due to low sintering temperature, $\alpha \rightarrow \beta$-Si_3N_4 phase transformation could not be observed. Both hardness and fracture toughness of the samples diminished with Si_3N_4 addition.

DECLARATION OF ETHICAL STANDARDS (ETİK STANDARTLARIN BEYANI)

The author of this article declares that the materials and methods they use in their work do not require ethical committee approval and/or legal-specific permission.

Bu makalenin yazarı çalışmalarında kullandıkları materyal ve yöntemlerin etik kurul izni ve/veya yasal-özel bir izin gerektirmediğini beyan ederler.

AUTHORS' CONTRIBUTIONS (YAZARLARIN KATKILARI)

***Sümeyra Ekşi*:** She conducted the experiments, analyzed the results and performed the writing process.

Gülsüm Topateş: She designed the study and experiments, supervised and performed the writing process.

Sümeyra Ekşi: Deneyleri yapmış, sonuçlarını analiz etmiş ve makalenin yazım işlemini gerçekleştirmiştir.

Gülsüm Topateş: Çalışmayı ve deneyleri tasarlamış, danışmanlık yapmış ve maklenin yazım işlemini gerçekleştirmiştir.

CONFLICT OF INTEREST (ÇIKAR ÇATIŞMASI)

There is no conflict of interest in this study.

Bu çalışmada herhangi bir çıkar çatışması yoktur.

REFERENCES (KAYNAKLAR)

[1] F. Mussano, T. Genova, L. Munaron, M.G. Faga, S. Carossa, Ceramic Biomaterials for Dental Implants: Current Use and Future Perspectives, Dent. Implant. and Biomat., 63 (2016) 63-78.

[2] C. Gautam, J. Joyner, A. Gautam, J. Rao, R. Vajtai, Zirconia Based Dental Ceramics: Structure, Mechanical Properties, Biocompatibility and Applications, Dalton Trans., 45 (2016) 19194-19215.

[3] B.D. Flinn, D.A. deGroot, L.A. Mancl, A.J. Raigrodski, Accelerated Aging Characteristics of Three Yttria-Stabilized Tetragonal Zirconia Polycrystalline Dental Materials, J. Prost. Dent., 108: 4 (2012) 223-230.

[4] P. Christel, A. Meunier, M. Heller, J.P. Torre, C.N. Peille, Mechanical Properties and Short-Term in Vivo Evaluation of Yttrium-Oxide-Partially-Stabilized Zirconia, J. Biomed. Mat. Res., 23:1 (1989) 45–61.

[5] L. Mihai, I. Parlatescu, C. Gheorghe, C. Andreescu, A. Bechir, M. Pacurar, C.N. Cumpaa, In vitro Study of the Effectiveness to Fractures of the Aesthetic Fixed Restorations Achieved from Zirconium and Alumina Rev. de Chim. Buch. Orig. Edit., 65 (2014) 65 725-729.

[6] T. Vagkopoulou, S. Koutayas, P. Koidis, J. Strub, Zirconia in dentistry: Part 1. Discovering The Nature of an Upcoming Bioceramic, Europ. J. Esthet. Dent., 4 (2019) 130-151.

[7] A.A. Madfa, F.A. Al-Sanabani, N.H. Al-Qudami, J.S. Al-Sanabani, A.G. Amran, "Use of Zirconia in Dentistry: An Overview" The Open Biomat .J., 5:1 (2014), 1-7.

[8] J. Singh, S. Singh, A. Verma, Artificial intelligence in use of ZrO_2 material in biomedical science". J. Electrochem. Sci.Eng., 13:1 (2023) 83-97.

[9] Y. Yanga, C. Hua, Q. Liub, J. Lia, Research progress and prospects of colored zirconia ceramics: A review, J. of Adv. Ceram., 13:10 (2024) 13, 1505-1522.

[10] O.A. Lukianova, V.V. Krasilnikov, A.A. Parkhomenko, V.V. Sirota, Microstructure and Phase Composition of Cold Isostatically Pressed and Pressureless Sintered Silicon Nitride, Nano. Res. Letters, 11:1 (2016) 148-154.

[11] M. Belmonte, Diamond Coating of Coloured Si_3N_4 Ceramics. Diamond Relat. Mater., 14:1 (2016) 54-59.

[12] I. Tanaka, G. Pezzotti, T. Okamoto, Y. Miyamoto, M. Koizumi, Hot Isostatic Press Sintering and Properties of Silicon Nitride without Additives, J. Am. Ceram. Soc., 72:9 (1989), 1656–1660.

[13] C.C. Guedes-Silva, A.C.D. Rodas, A.C. Silva, C.Ribeiro, F.M.S Carvalho, O.Z. Higa, T.S. Ferreira, Microstructure, Mechanical Properties and in vitro Biological Behavior of Silicon Nitride Ceramics, Mater. Res., 21:6 (2018), 1-12.

[14] A. Neumann, T. Reske, M. Held, K. Jahnke, C. Ragoss, H.R. Maier, H. R. , Comparative investigation of the biocompatibility of various silicon nitride ceramic qualities in vitro, J. Mater. Sci. Mater. Med., 15 (2004) 1135-1140.

[15] M. Rahaman, W. Xiao, Silicon Nitride Bioceramics in Healthcare. Int. J. Appl. Ceram. Technol., 15:4 (2017) 861–872.

[16] A. Pechenik, G.J. Piermarini, S.C. Danforth, Fabrication of Transparent Silicon Nitride from Nanosize Particles. J. Am. Ceram. Soc., 75:12 (1992) 3283-3288.

[17] N. Nishiyama, R. Ishikawa, H. Ohfuji, H. Marquardt, A. Kurnosov, T. Taniguchi, T., et al. Transparent Polycrystalline Cubic Silicon Nitride, Sci. Rep., 7 (2017) 44755- 44763.

[18] G. Pezzotti, Silicon Nitride: A Bioceramic with a Gift, ACS Appl. Mater. Inter., 11:30 (2019) 26619-26636.

[19] L. Fu, H. Engqvist, W. Xia, Spark Plasma Sintering of Biodegradable Si_3N_4 Bioceramic with Sr, Mg and Si as Sintering Additives for Spinal Fusion, J. Europ. Ceram. Soc., 38:4 (2017) 2110-2119.

[20] H. Mohammadi, S. Beddu, M. Petrů, M. Sepantafar, M. Ebadi, B.K. Yap, et al. Advances in silicon nitride ceramic biomaterials for dental

applications–A review, J.Mater. Res. Techn., 28 (2023) 2778-2791.

[21] A.S. Buyakov, Y.A., Mirovoy, A.Y. Smolin, S.P. Buyakova, S. P. Increasing fracture toughness of zirconia-based composites as a synergistic effect of the introducing different inclusions, Ceram. Int., 47:8 (2001) 10582-10589.

[22] N.F. Amat, A. Muchtar, M.S. Amril, M.J. Ghazali, N. Yahaya, Effect of sintering temperature on the aging resistance and mechanical properties of monolithic zirconia, J. Mater. Res. Technol., 8:1 (2019) 1092-1101.

[23] E.M.M Ewais, M.A.A. Attia, A. Abousree-Hegazy, A., R.K. Bordia, Investigation of the Effect of ZrO_2 and ZrO_2/Al_2O_3 Additions on the Hot-Pressing and Properties of Equimolecular Mixtures of α- and β-Si_3N_4, Ceram. Int., 36:4 (2019) 1327-1338.

[24] B. Matovic, Low Temperature Sintering Additives for Silicon Nitride, PhD Thesis, Max-Planck-Institut für Metallforschung, (2003) Stuttgart, 90.

[25] S. Chockalingam, V.R. Amarakoon, 2.45 GHz microwave sintered Si_3N_4-ZrO_2 composites, J. Ceram. Soc. Jpn., 116:6 (2008) 700-705.

[26] H.X. Li, J.K. Yu, K. Hiragushi, Y. Kayano, Y. Mizota, Phase composition of TiO_2-coated ZrO_2/Si_3N_4 composite. J. Europ. Ceram. Soc., 19:3 (1999) 299-303.

[27] W.A. Sanders, D.M. Mieskowski. Strength and Microstructure of Si_3N_4 Sintered with ZrO_2 Additions, Adv. Ceram. Mater., 1:2 (1986), 66-173.

[28] H.J. Kleebe, G. Pezzotti, G. Ziegler, G. Microstructure and fracture toughness of Si_3N_4 ceramics: combined roles of grain morphology and secondary phase chemistry, J. Am. Ceram. Soc., 82:7 (1999) 1857-1867.

[29] A. Sayyadi-Shahraki, S.M. Rafiaei, S. Ghadami, S., K.A. Nekouee, Densification and Mechanical Properties of Spark Plasma Sintered Si_3N_4/ZrO_2 Nano-Composite, J. Alloys Compd., 776 (2019), 1-32.

[30] G-X. Mao, J-M. Wu, C. Tian, C-L. Liu, L. Guo, W.H Cai, Shi, Y.S. ZrO_2 reinforced porous Si_3N_4-based ceramics with improved mechanical properties fabricated via vat photopolymerization (VPP), Add. Manufac., 91 (2024) 104327.