

THE FLUORINE EFFECT ON THE GRAIN-GROWTH OF α^1 : β^1 -SiAlON CERAMICS

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ABSTRACT

SiAlON ceramics are of major interest for industrial applications due to their excellent mechanical properties. The starting Si_3N_4 powder (α or β), the type of sintering additive and sintering conditions govern the microstructural evolution of SiAlON ceramics. In this study, α^1 : β^1 SiAlON ceramics with an equal mole intergranular phase content, different type cation systems (Y:Sm:Ca and Ca:Ce) with different molar ratio (30:64:6 and 33:67) were produced by using coarse ($d_{50}=1\ \mu\text{m}$) β - Si_3N_4 powder. CaF_2 and CaCO_3 were utilized as Ca sources. Despite the fact that α^1 -SiAlON phase cannot be stabilized in Ca:Ce (CaCO_3 as a Ca source) system, α^1 -SiAlON phase stability and unpredictable α^1 -SiAlON grain-growth in both a and c directions was achieved when CaF_2 was incorporated in the composition. On the other hand, an increase in α^1 -SiAlON amount and more elongated SiAlON grain evolution was observed when CaF_2 was used instead of CaCO_3 in Y:Sm:Ca cation system. Furthermore, using CaF_2 instead of CaCO_3 gave rise to an increase in densities. Therefore, the substantial effect of CaF_2 on abnormal grain growth and α^1 -SiAlON phase stabilization was observed.

Keywords: Fluorine, Grain growth, α^1 -SiAlON stability, Microstructure

1. INTRODUCTION

Microstructure evolution of silicon nitride based ceramics is controlled by properties of initial Si_3N_4 powder, sintering additives and sintering conditions. Composition and particle size of starting Si_3N_4 powder have been known to have a significant effect on microstructure development. Generally two forms of silicon nitride powders: α - Si_3N_4 and β - Si_3N_4 are used as a starting powder. Wild and co-workers [1] have shown that a small amount of oxygen is incorporated into the atomic structure of the α phase; the approximate formula is $\text{Si}_{11.5}\text{N}_{15}\text{O}_{0.5}$, whereas the β -phase is pure β - Si_3N_4 . Thus α - Si_3N_4 powder is used more common due to higher reactivity than β - Si_3N_4 powder. It is well known that α phase is low temperature configuration of Si_3N_4 and transform to β -phase at $\sim 1410^\circ\text{C}$ [2]. Other reason for the preference of α - Si_3N_4 powder is elongated β grain formation after $\alpha \rightarrow \beta$ phase transformation [3]. However, fine α - Si_3N_4 powders are expensive and this is a key problem for large scale applications. When β - Si_3N_4 powder is used as a starting powder, elongated grain formation and densification are rather difficult due to aforementioned reasons [4]. On the other hand, β - Si_3N_4 powders can be produced in an economic route with combustion synthesis [5]. Use of such powders may open up possibilities for wider applications of SiAlON ceramics.

The second parameter on microstructure evolution is type of sintering additives. Most of the investigations had been focused on the influence of sintering additives on grain growth [6,7]. The understanding of grain growth kinetics is a key issue in order to design high toughness and high strength materials. It is generally accepted that grain growth anisotropy increase with increasing cation size due to preferred segregation of large cations on the prism plane of grains [8,9]. Besides, sintering additives have an effect on intergranular phase chemistry [10]. In SiAlON ceramics, the influence of cations on the interfacial properties is rather different than Si_3N_4 ceramics since some Al^{3+} cations enter into the crystal structure or/and remain in the intergranular phase. The third important parameter is sintering

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condition. Today silicon nitride ceramics are densified by pressureless sintering, gas pressure sintering, hot pressing or hot isostatic pressing. Gas pressure sintering of Si_3N_4 ceramics at higher temperatures ($>1800^\circ\text{C}$) develops an in situ composite microstructures with a high fracture toughness [11].

There exist some studies on microstructural evolution of SiAlON ceramics when use of $\beta\text{-Si}_3\text{N}_4$ as a starting powder [12-14]. However there is no study on the effect of CaF_2 sintering additive on microstructural evolution of SiAlON ceramics. In this respect this study is novel. Therefore the aim of this study is to evaluate the effect of fluorine on SiAlON grain growth as well as to correlate this α' -SiAlON phase stability and sample density.

2. MATERIALS AND METHOD

The starting $\beta\text{-Si}_3\text{N}_4$ powder (Beijing Chanlian-Dacheng Trade Co., Ltd., China) was produced by combustion synthesis and consisted 100% $\beta\text{-Si}_3\text{N}_4$ phase. Table 1 provides the specification of as-received and milled $\beta\text{-Si}_3\text{N}_4$ powder, which contains 3 wt.% oxygen. Primary particle size of $\beta\text{-Si}_3\text{N}_4$ powder was measured to be around 10 μm by laser diffraction method (Figure 1). Attrition milling in water was performed to decrease the average particle size of $\beta\text{-Si}_3\text{N}_4$ starting powder to 1 μm . The corresponding starting powder was designated as B1. The particle size distribution graph of B1 powder was given in Figure 2. Representative SEM images of as-received and milled $\beta\text{-Si}_3\text{N}_4$ powders and XRD analysis of starting $\beta\text{-Si}_3\text{N}_4$ powders are shown in Figure 3 and 4, respectively. Starting powder contains Fe, Fe_2Si , FeSi_2 and Si as a major impurity.

Table 1. Specifications of $\beta\text{-Si}_3\text{N}_4$ powders

Starting Powders	B (as-received)	B1
$\alpha:\beta$ Phase Ratio	100 β	100 β
d_{50} (μm)	10	1.2
d_{90} (μm)	36	2.4
d_{10} (μm)	2.4	0.5
Milling time (hr)	-	9

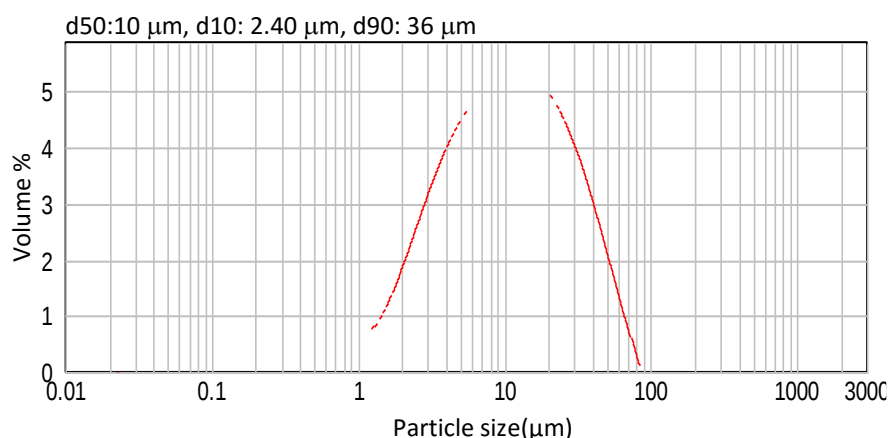


Figure 1. Particle size distribution graph of as-received $\beta\text{-Si}_3\text{N}_4$ powder

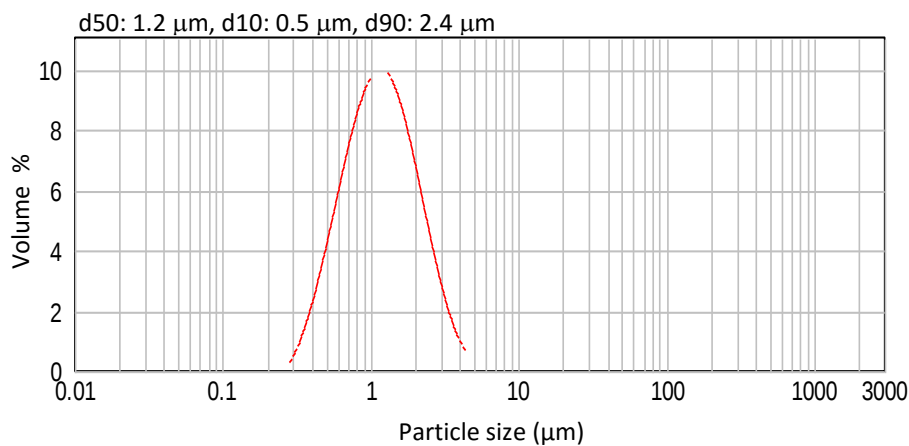


Figure 2. Particle size distribution graph of B1 powder

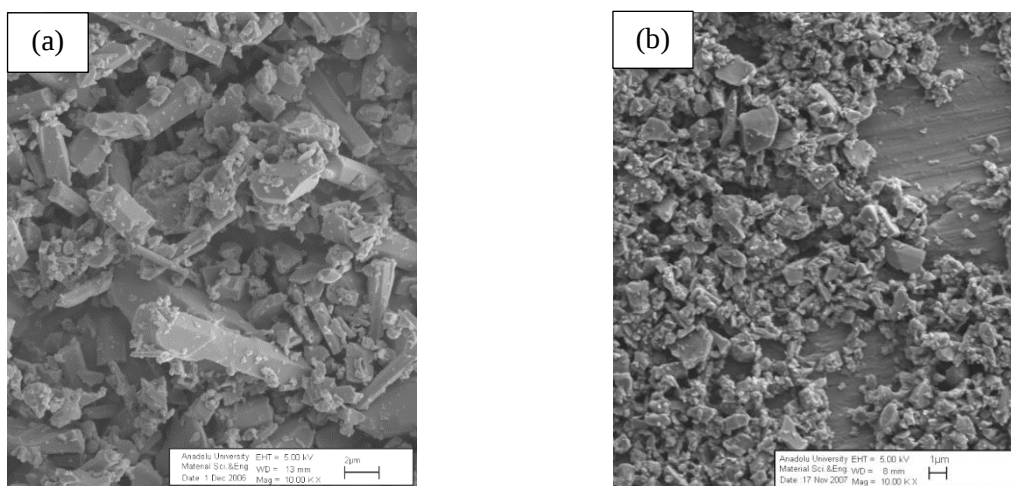


Figure 3. SE-SEM images of (a) as-received β -Si₃N₄ powder (b) B1 powder

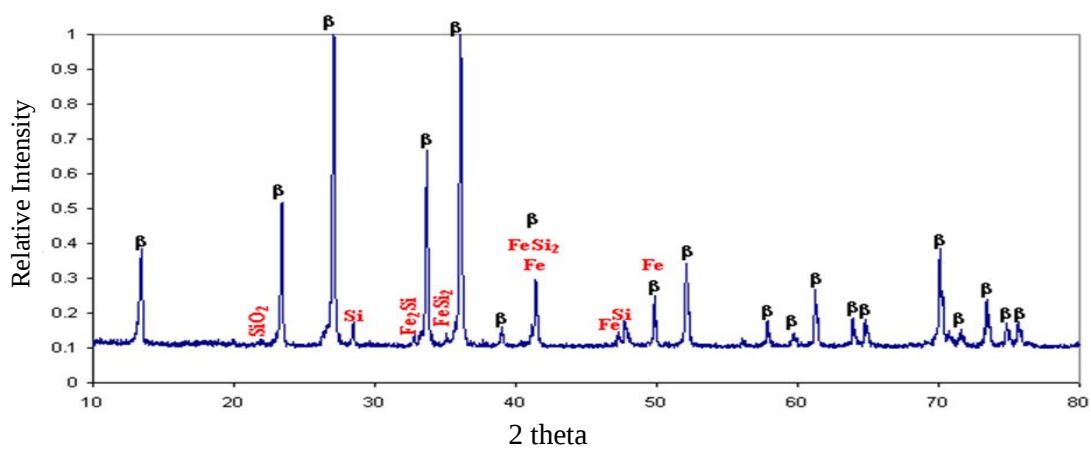


Figure 4. XRD spectra of as-received β -Si₃N₄ powder (β : β -Si₃N₄)

30 α' :70 β' SiAlON composition was designed where hardness of α' -SiAlON and toughness of β' -SiAlON wanted to be utilized. Y:Sm:Ca and Ca:Ce multi cation systems with different molar ratio (30:64:6 and 33:67) were chosen. High purity AlN powder (H Type, Tokuyama Corp. Japan) containing 1.6 wt% O, Al₂O₃ (Alcoa A16-SG, Pittsburgh, USA), Y₂O₃ (>99.99%, Treibacher, Austria), Sm₂O₃ (>99.9%, Stanford Materials Corp., USA), CeO₂ (>99.99%, Aldrich, Germany), CaCO₃ (>99.75%, Reidel-de Haen, Germany) and CaF₂ (>99.99%, Aldrich, Germany) were used as sintering additives. Y-Sm- Ca and Ca-Ce multi cation doping systems were chosen with the aim to produce self reinforcement microstructures. CaO was used to avoid α' to β' -SiAlON transformation, Y₂O₃ and/or Re₂O₃ (where ZRe>62)) to increase the stability and hardness of α' -SiAlON and Sm₂O₃/CeO₂ (where ZRe<62) to develop elongated β' -SiAlON grains to increase fracture toughness.

The formulated composition contains high enough liquid phase (0.033 moles) to provide easy densification. Theoretical liquid phase content was calculated take into account the amount of sintering additives in the composition. However, to prevent the side effect of intergranular phase, refractory melilite (Ln₂Si_{3-x}Al_xO_{3+x}N_{4-x}) phase crystallization was aimed. Designed SiAlON compositions were prepared by planetary milling for 90 min at 300 rpm in isopropyl alcohol using Si₃N₄ balls. The slurries were then dried in a rotary evaporator and sieved through 75 μ m. The powders were uniaxially pressed at 25 MPa, 15mm ϕ and 4 mm in thicknesses and subsequently cold isostatically pressed at 300 MPa to improve green density. The pellets were sintered using a two-step gas pressure sintering cycle. In the case of one step sintering, gas remains in the pores and effect the densification negatively. Therefore in the first step must be reached to closed pores level at certain nitrogen pressure to prevent Si₃N₄ decomposition and then should go up to high pressures to promote the densification. The first step is called as pre-sintering and was carried out at 1900°C for 60 min, 0.5 MPa nitrogen gas pressure and second step at 1940 °C for 120 min of 2.2 MPa nitrogen gas pressure and then the furnace was allowed to cool at a rate of 5°C/min.

Archimedes principle was used to measure the bulk density of samples after sintering. Theoretical density of samples was found by He gas picnometer. %T.D. values were calculated with following equation.

$$\% \text{ Theoretical Density} = (\text{Bulk density} / \text{Theoretical density}) * 100 \quad (1)$$

The types of crystalline phases and the α' : β' -SiAlON phase ratios were determined by means of X-ray diffraction analyses (XRD-Rigaku, Cu-K α radiation). The α' : β' -SiAlON phase ratios were found by quantitative estimation from the XRD patterns using the integrated intensities of the (102) and (210) reflections of α' -SiAlON and the (101) and (210) reflections of β' -SiAlON by the following equation:

$$\frac{I_{\beta}}{I_{\beta} + I_{\alpha}} = \frac{1}{1 + K \left[\left(\frac{1}{w_{\beta}} \right) - 1 \right]} \quad (2)$$

where I_{α} and I_{β} are observed intensities of α' and β' -SiAlON peaks, respectively, w_{β} is the relative weight fraction of β' -SiAlON, and K is the combined proportionality constant resulting from the constants in the two equations, namely:

$$I_{\beta} = K_{\beta} * W_{\beta} \quad (3)$$

$$I_{\alpha} = K_{\alpha} * W_{\alpha} \quad (4)$$

which is (0.518 for β (101) – α (102) reflections and 0.544 for β (210) – α (210) reflections [17]. The lattice parameters of SiAlONs were measured with silicon powders as the internal standard. Lattice parameters are calculated according to following formula, where d is the distance between the planes, a and c are lattice parameters. Calculation was done by using (101) and (210) planes.

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (5)$$

The samples were prepared before SEM examination. Cold moulded specimens were subjected to grinding and polishing processes. Grinding of sample was carried out with abrasive papers with grid size of 200, 400, 600, 800 and 1000 respectively. Subsequently, polishing of sample was made by tetrapol device by using DAC and NAP clothes with its unique suspension. Time for DAC 5 min and for NAP 3 min. After each step the surfaces of the samples were treated with metylalcohol and dried with air blowing. Polished surfaces of the sintered samples were gold coated prior to examination in a Zeiss VP50-Supra type scanning electron microscope (SEM) by using back-scattered electron imaging mode.

3. RESULTS AND DISCUSSION

The results of phase analysis, bulk density, and theoretical density and weight losses are given in Table 2. >%99.75 theoretical density was achieved in all compositions. Considerably high (≥ 2.19 %) weight losses was observed due to impurities in initial β - Si_3N_4 powder. By using CaF_2 instead of CaO , bulk densities increased %0.6-0.7 and weight losses %34-60. F in structure is evaporated as a SiF_4 and hence this phenomena lead to more weight losses [18,19].

In Ca:Ce cation sytem, α' -SiAlON phase stability was not achieved (100 β' -SiAlON) employing CaO in Ca:Ce containing composition. Use of CaF_2 instead of CaO resulted in 81 β' :19 α' -SiAlON phase composition. Designed phase ratios (70 β' :30 α') was not achieved in both cases (Figure 5). Clarke stated that [20] if initial Si_3N_4 powder include Cl/F as a impurity, $\alpha \rightarrow \beta$ - Si_3N_4 phase transformation retarded considerably. Chlorine remains structure as a silisiumchlorid form until 1750°C and so stabilize α - Si_3N_4 phase.

There are three approaches why α' -SiAlON phase stability was achieved in the case of employing CaF_2 instead of CaO . The first one is decrease in oxygen content in intergranular phase may result in α' -SiAlON phase stability [21]. $\alpha' \leftrightarrow \beta'$ -SiAlON phase transformation depends on starting composition, type of sintering additives, viscosity of liquid phase and liquid phase content [22]. Excess oxygen in the liquid phase causes a decrease in the viscosity of the liquid phase and hence provides $\alpha' \leftrightarrow \beta'$ -SiAlON phase transformation. Previously $\alpha' \rightarrow \beta'$ -SiAlON phase transformation was observed in Ca- α' -SiAlON and Y- α' -SiAlON systems [23].



chemical reactions may progress depending on liquid phase composition. Besides, $\alpha' \rightarrow \beta'$ -SiAlON phase transformation between 1300-1600°C occurred during slow cooling rates [24]. In this study, a slow cooling regime with 5°C/min. was applied. Therefore $\alpha' \rightarrow \beta'$ -SiAlON phase transformation is possible.

Table 2. Densification and phase analysis results of SiAlON samples (%T.D.: percent theoretical density, %W.L: percent weight losses, IGP: Intergranular phase)

Cation system	Sintering Additives	Bulk Density (gr/cm ³)	%T.D.	%W.L.	β' : α' Ratio	IGP Chemistry	Lattice Parameters
Y:Sm:Ca (30:64:6)	Y ₂ O ₃ Sm ₂ O ₃ CaO	3.3518	99.90	2.19	73 β' :27 α'	Melilite	a: 7.6192±0.0022 c: 5.7082±0.0023
Y:Sm:Ca (30:64:6)	Y ₂ O ₃ Sm ₂ O ₃ CaF ₂	3.3715	99.99	2.94	68 β' :32 α'	Melilite	a: 7.6192±0.0012 c: 5.7082±0.0014
Ca:Ce (33:67)	CaO CeO ₂	3.2369	99.75	3.33	100 β'	Amorphous	a: 7.6210±0.0015 c: 5.7027±0.0018
Ca:Ce (33:67)	CaF ₂ CeO ₂	3.2593	99.99	5.30	81 β' :19 α'	Amorphous	a: 7.6210±0.0021 c: 5.7027±0.0022

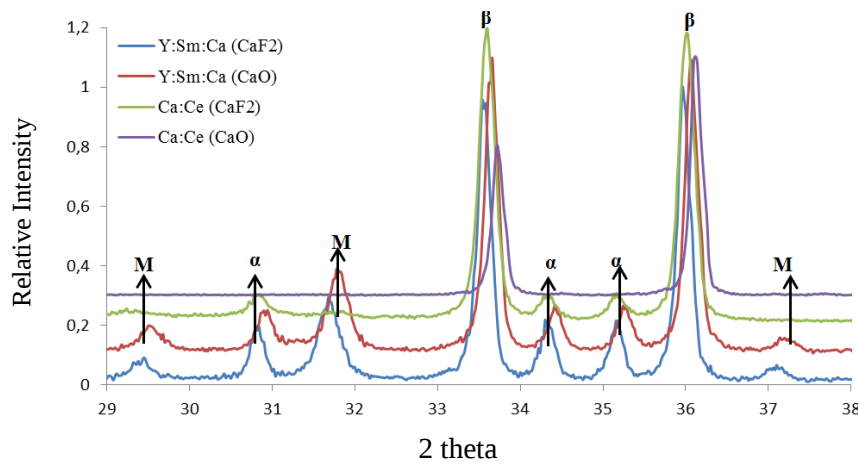


Figure 5. XRD graph of SiAlON samples (α : α' -SiAlON, β : β' -SiAlON, M: Melilite phase)

The second approach is CaF₂ addition may cause more Ca substitution in α' -SiAlON crystal structure as evidenced by the increase in the density of samples from 3.2369 to 3.2593 gr/cm³. Since no pores were observed in microstructural observations, this is an evidence of entering more Ca in the case of CaF₂ addition.

The third and last approach is, CaF₂ may provide more α' -SiAlON phase seeding since its melting temperature is lower as compared to CaO (1423°C for CaF₂ and 2572°C for CaO) and so it lowers eutectic temperature and viscosity in oxynitride liquid phase. Although Ce cation is known as a nitrogen rich melilite phase stabilizer, melilite phase crystallization was not achieved whether CaF₂ or CaO was used in equimolar Ca and Ce.

Since Y:Sm:Ca dopant system include less CaO/CaF₂ content compared to Ca:Ce system, ~%20 increase (27 α →33 α) in α' -SiAlON phase amount was observed when using CaF₂ instead of CaO. Melilite phase crystallization was provided in both materials (including CaO/CaF₂), due to high Sm content (64%). Increase in α' -SiAlON phase content may be resulted from substitution of more Ca in the case of using CaF₂ powder. In order to prove this phenomenon a and c crystal parameters were calculated. However it was observed that a and c parameters were similar.

SEM images CaO or CaF₂ used Y:Sm:Ca doped SiAlON samples were given in Figure 6. The microstructure of the samples revealed the presence of three different contrasting phases. The prismatic grains with darker contrast were β' -SiAlON, the equiaxed grains with grey contrast were α' -SiAlON and small white areas were intergranular phase due to the strong electron-scattering characteristic of

the heavy metals. Increase in α' -SiAlON content was observed with addition of CaF_2 . β' -SiAlON grains turned into more elongated morphology when CaF_2 was used instead of CaO contrary to α' -SiAlON grains was getting more equiaxed shape.

Regarding Ca:Ce doped SiAlON composition, despite the fact that α' -SiAlON phase cannot be stabilized in Ca:Ce (CaCO_3 as a Ca source) system, α' -SiAlON phase stability and unpredictable α' -SiAlON grain-growth in both a and c directions was easily achieved (Figure7). The grain growth mechanism of α' -SiAlON is related to liquid phase content and viscosity. In this case addition of CaF_2 may lead to decrease in viscosity of liquid phase and provide effective mobility of atoms in liquid phase. CaF_2 addition didn't provide abnormal grain growth in Y:Sm:Ca doped SiAlON. This case may be resulted from the difference in viscosity of liquid phase, in both (Ca:Ce and Y:Sm:Ca) cation system.

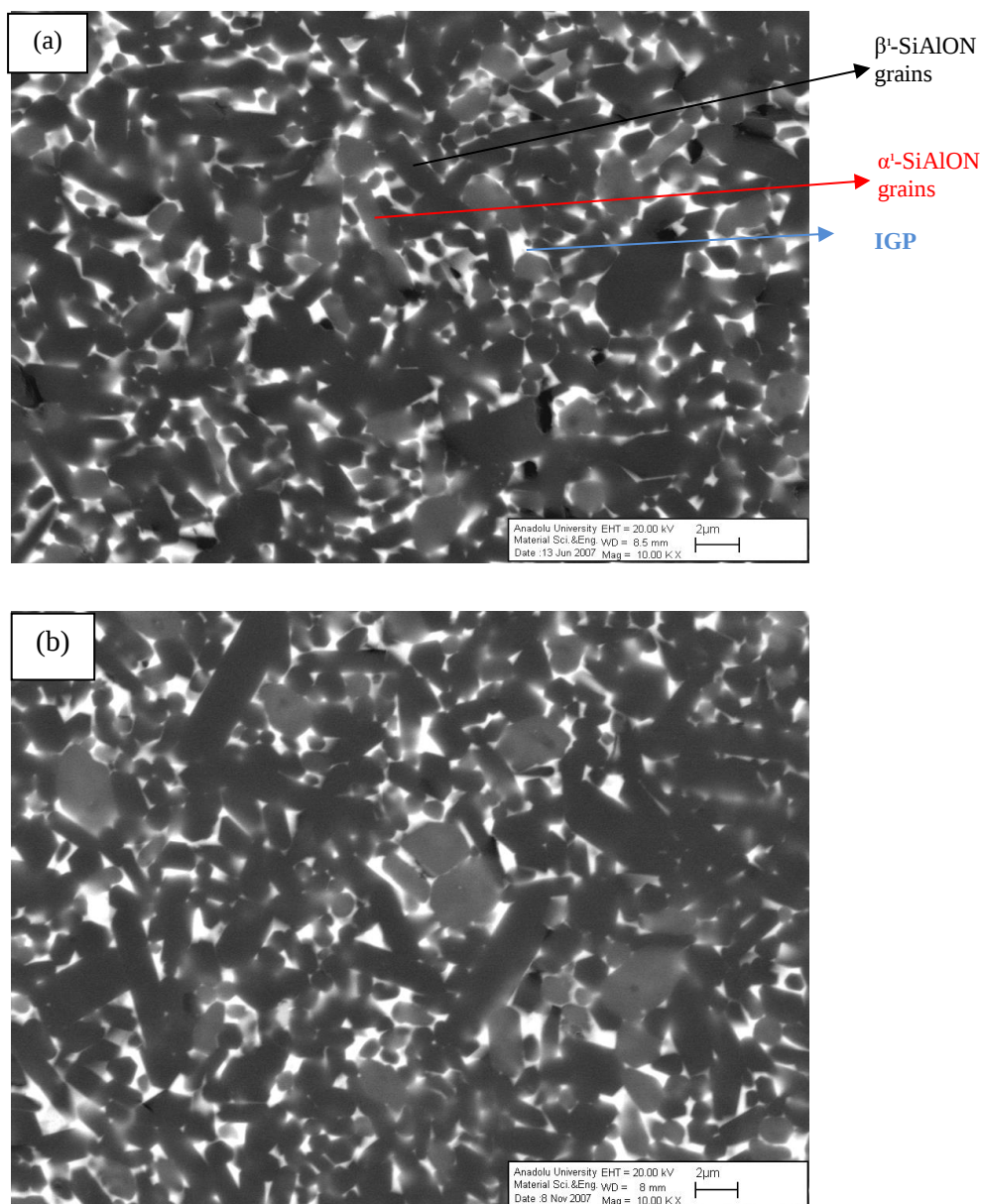


Figure 6. Representative BSE-SEM images of Y:Sm:Ca doped SiAlON with (a) CaO and (b) CaF_2 as a Ca source

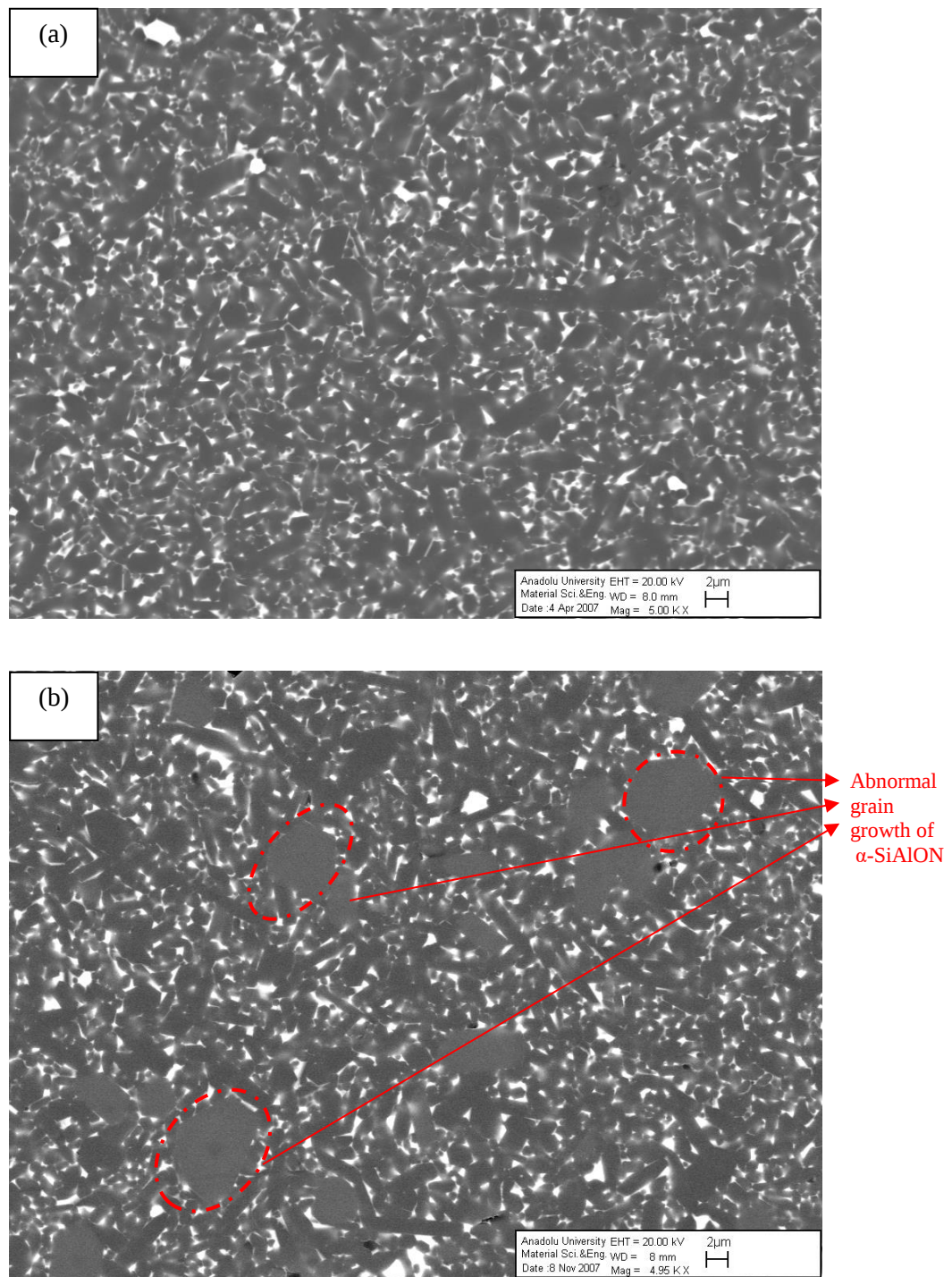


Figure 7. Representative BSE-SEM images of Ca:Ce doped SiAlON with (a) CaO and (b) CaF₂ as a Ca source

4. CONCLUSIONS

This study contains results of original research work on the effect of CaF_2 on α' -SiAlON phase stability, abnormal grain-growth, intergranular phase chemistry and density in α' : β' -SiAlON ceramics. Based on the experimental results and observations, the following conclusions were drawn:

1. Despite the fact that α' -SiAlON phase cannot be stabilized in Ca:Ce (CaCO_3 as a Ca source) system, α' -SiAlON phase stability and unpredictable α' -SiAlON grain-growth in both a and c directions was easily achieved when CaF_2 was incorporated in the composition. On the other hand, an increase in α' -SiAlON amount and more elongated SiAlON grain evolution was observed when CaF_2 was used instead of CaCO_3 in Y:Sm:Ca cation system.
2. The use of CaF_2 instead of CaCO_3 gives rise to an increase in densities in both cation systems.
3. Although Ce cation is known as a nitrogen rich melilite phase stabilizer, melilite phase crystallization was not achieved whether CaF_2 or CaO was used in equimolar Ca and Ce.

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