



Preparation of Reaction Bonded Silicon Nitride (RBSN) through commercial silicon gel-casting and investigation the effect of premix pH and sintering aid compounds on silicon nitride formation and porosity body

Mehri Mashhai¹, Mahboubeh Vaseghi^{2*}, Reihaneh Ahmadi³

1-Associate Professor, Faculty of Materials and Manufacturing, Malek Ashtar University of Technology, Tehran, Iran

*2-Assistant Professor, Materials and Energy Research Center, Dezful Branch, Islamic Azad University, Dezful, Iran

3-MS, Faculty of Materials and Manufacturing, Malek Ashtar University of Technology, Tehran, Iran

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ABSTRACT

In this study, porous Si_3N_4 ceramic were prepared by a gel-casting silicon route and under nitrogen atmosphere with pressureless sintering. It was found that the preparation of sol in acid pH ($\text{pH} \sim 2-3$) than alkaline pH ($\text{pH} \sim 11-12$) improved in terms of Si_3N_4 development and the Si residue not participating. Moreover, in employing sintering aid, a higher amount of SiO_2 to Al_2O_3 and Y_2O_3 was more effective in the development of $\beta\text{-Si}_3\text{N}_4$ grains, and denser ceramic with less porosity were obtained using Y_2O_3 0.8 wt%, Al_2O_3 2.5 wt%, and SiO_2 6.5wt% with a porosity of 22.1% and density of 2.61 g.cm^{-3} .

Corresponding Author Email: m_vaseghi83@yahoo.com, ORCID: 0000-0002-6354-772X

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1. INTRODUCTION

Silicon nitride (Si_3N_4) is a low-density ceramic that can be used at high temperatures. These premium ceramics work extremely well against thermal shocks and due to good oxidation resistance, excellent wear resistance, acceptable fracture toughness, and high compressive strength, they are used in various applications, including missile nose, engine and turbocharger components, cutting tools, and bearings [1-3]. The strong covalent bonding of Si-N in Si_3N_4 prevents the atomic transfer in grains boundary during sintering. Sintering at high temperatures and for a long time, in addition to high energy consumption, causes high shrinkage of porous ceramics. In general, it is not an easy task to fabricate high-quality Si_3N_4 porous ceramics [4]. Using conventional methods to produce Si_3N_4 requires a lot of energy and time. For this purpose, one should use high-temperature furnaces that can perform time-consuming processes [5]. This, in turn, incurs extra costs, hindering the industrial application of this valuable ceramic material [6]. Therefore, reaction-bonded silicon nitride (RBSN) is a cost-effective Si_3N_4 ceramic solution with favorable physical and mechanical properties. In the RBSN method, the low cost of Si powder and appropriate product mechanical properties, low thermal conductivity, and low shrinkage during the sintering procedure are already expanding the application of this wonderful

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material as both structural and functional compounds in various industries [6,7,8,9]. If Si_3N_4 powder is used to make silicon nitride parts, high temperatures (higher than 1750°C) and pressure are needed for sintering, but it decomposes into silicon and nitrogen at temperatures higher than 1880°C [10]. Except in exception cases, it is unavoidable to use the help of sintering aid such as alumina and silica to sinter the silicon nitride parts at a lower temperature and to help the growth of beta grains [6,11,12]. Liquid phase sintering (LPS) by using metal oxides as the sintering aid promotes atomic transport [13,14] and Increases the probability of nucliation and growth of $\beta\text{-Si}_3\text{N}_4$ [14] The basis of the gel-casting method is the mixing of organic monomers that are polymerized in situ [15,16, 17]. In this method, it is very important to prepare a homogeneous slurry of solid particles that has a suitable viscosity [11,18,19] So after gelling, bodies are made that are close to the final shape and have a uniform structural homogeneity, which has high strength in the raw state [20,21].

The present study was an attempt to further improve the gel-casting procedure in manufacturing porous Si_3N_4 ceramics. To reduce the costs of manufacturing silicon nitride ceramics, a combination of silicon bodies formed through the gel-casting method followed by a direct nitridation process was employed to manufacture a porous silicon nitride body. To investigate the influence of suspension pH on the formation of silicon nitride, suspension was prepared in acidic and alkaline pH. Additionally, the effect of SiO_2 , Al_2O_3 , and Y_2O_3 as the sintering aid on RBSN development and the formation of the Si_3N_4 was investigated.

2. MATERIALS AND METHODS

2.1. Raw Materials

Commercial Si powder (purity $\geq$ 99.5%, $d_{50} = 2 \mu\text{m}$) was used as the main powder. Also, Al_2O_3 (mean particle size: $0.5 \mu\text{m}$, China), SiO_2 (Quartz, $d_{50} = 1 \mu\text{m}$, Riedel, Germany), and Y_2O_3 (purity $\geq$ 99.9 wt%; $d_{50}=0.5\mu\text{m}$, China) were used as sintering aid. Table 1 shows the designation of the samples and their compositions in the study.

TABLE 1. Composition of the starting powders

Sample code	Si (wt%)	Al_2O_3 (wt%)	Y_2O_3 (wt%)	SiO_2 (wt%)
60A*	100	0	0	0
60B*	100	0	0	0
AYS1	90	4.5	1.5	4
AYS2	90	3.5	1.1	5.5
AYS3	90	2.5	0.8	6.5

*Samples A and B were prepared in monomeric solutions with acid and alkaline pH, respectively

2.2. Preparation of premix and gel-casting

The gel-casting procedure followed that described in our previous work [22]. deionized water, Acrylamide (AM), and methylene bisacrylamide (MBAM) were used as the solvent, networker monomer, and cross-linker, respectively. Also, Ammonium persulfate (APS), Tetramethylethylenediamine (TEMED), and Tetramethylammonium hydroxide (TMAH) were used as initiators, catalysts, and dispersants, respectively. To prepare a slurry containing solid loading, deionized water, 0.3 wt% dispersants (TMAH), and a mixture of the (AM) and (MBAM) with an AM/MBAM ratio (of 15:1 respectively) and the content ratio of 24 wt% were mixed. The ceramic powders as detailed in Table 1, were mixed and homogenized before they were added to the premix solution. The was placed in a planetary ball mill to homogenize for 30 min, and HCl and ammonia solution 28% (Merck) were used to adjust its pH. Deaerating the suspension was completed in about 5 minutes using a vacuum pump

with a pressure of 10-17 torr. The initiator (APS) and the catalyst (TEMED) were then added to the slurry, which was immediately cast into a mold. Then, the samples were removed from the mold and dried for 48hrs. Finally, the gel samples were heated up to 1350°C for nitridation and sintering. The entire heating operation time in the tube furnace (TF5/25) was 1340 minutes (~22hr) under nitrogen %99.99 flow with a minimum rate of 1 liter per hour. Figure. 1 shows the flow chart of the preparation for the sample by aqueous gelcasting using.

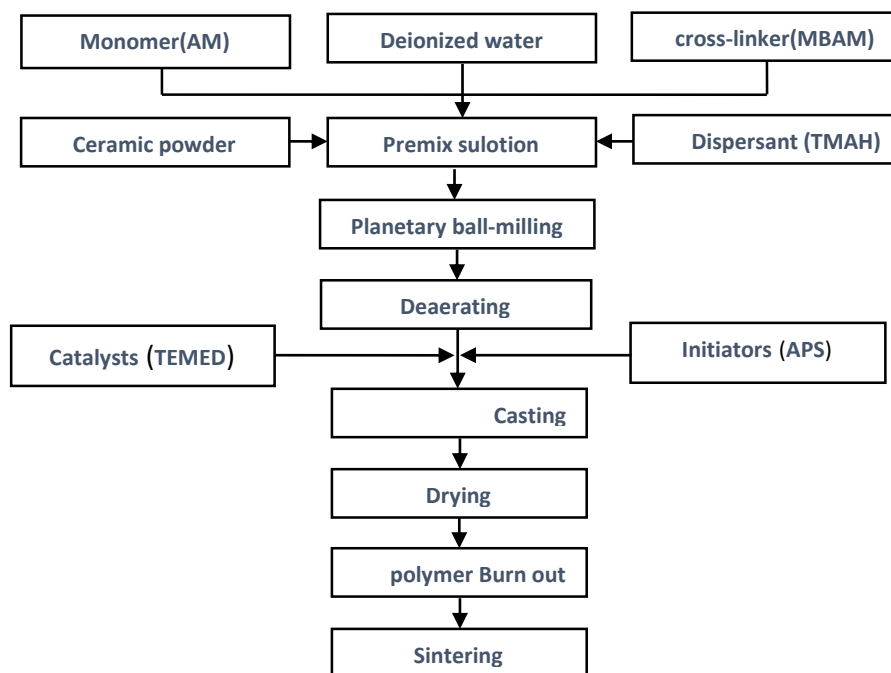


Figure 1. the flow chart of the preparation for the sample by aqueous gelcasting using

2.3. Characterization

An X-ray diffractometer (Siemens, D-500) CuK α radiation was used to identify the phases. Also, scanning electron microscopy (MIRA TESCAN) was used to observe the sintered samples' microstructures. In addition, the Archimedes Method (based on ASTM C20-00 standards) was followed to assay the bulk density and apparent porosity of the sintered bodies with deionized water used as the liquid medium. The heating regime of sintering is shown in Figure 2.

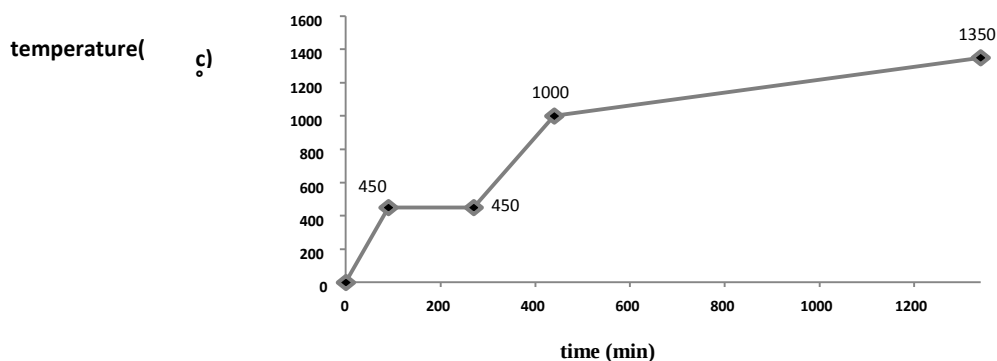


Figure 2. The heating regime of the gel samples under nitrogen gas flow

3. RESULTS AND DISCUSSION

3.1. Effect of pH of the monomer solution

Figure 3 shows the XRD results of the samples sintered at 1350°C. Three phases, namely β - Si_3N_4 , Si, and Cristobalite were identified in the samples within the XRD analysis range using PDF2 standard cards of 96100-1246, 00-027-1402, and 96-900-1579, respectively. The XRD pattern indicates that Si_3N_4 was crystallized as β phase at about 1350°C.

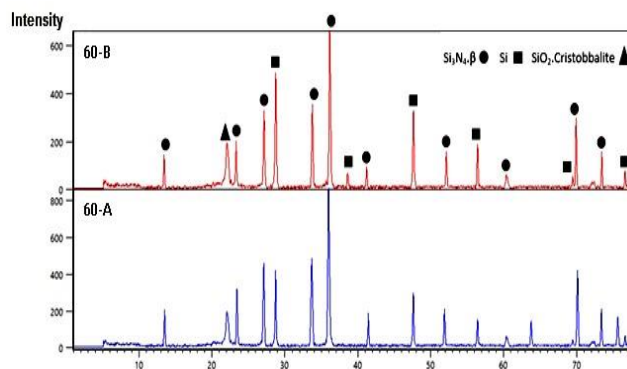


Figure 3. XRD patterns of samples 60-A and 60-B

As shown in Figure 4, the lowest ΔG at temperatures 1200-1450°C is related to the reaction of silicon and nitrogen [23]. Therefore, Si_3N_4 is formed as a result of the reaction of Si and N at a temperature of 1350°C. Below are the equations related to each graph [23].



Also, since Si_3N_4 nucleating agents were not used in the samples, the sintering temperature was considered to be lower than the silicon melting temperature (1412 °C) To prevent the melting of silicon at a temperature higher. A second phase identified from the XRD peaks (Figure 3) is the metallic silicon remaining from the raw material that did not engage in the reaction.

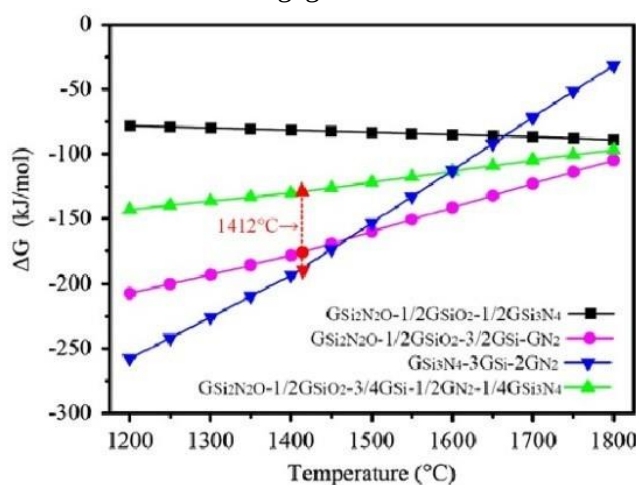


Figure 4. Gibbs free energy change in Si-SiO₂-N₂ system reactions as a function of temperature [19]

Typical in nitridation reactions nitriding reactions carried out at the temperature of 1350°C, there is always some metallic silicon phase on the surface or inside the grains along with the formation of main phases [23]. Of course, the usual temperature in the RBSN method is 1200-1450°C which is performed the post-heat treatment for the grain growth of the formed Si₃N₄ phases [24].

Another phase identified in the study was cristobalite (SiO₂). The cristobalite phase is semi-permanent below 1300°C [25]. There is usually SiO₂ on the surface of Si particles. When the temperature is around 1300, cristobalite phase nucleation starts heterogeneously, and cristobalite grains grow with temperature increases [23].

Samples 60A and 60B were prepared under similar conditions while their suspensions were prepared under acid and alkaline conditions, respectively. their identified phases at XRD peaks are shown in Figure 2. A comparison of the X-ray diffractions of samples 60A and 60B showed that in an acid environment, the intensity of the beta silicon nitride phase increased while the metallic Si phase decreased as compared with the alkaline environment. The electric charge appears due to the reaction of SiO₂ in acid and alkali media. As a result, Si(OH) groups are formed in the acidic environment [26]. Then Si is available on the free surface and has a high tendency to hydrolyze in water. Therefore, when the silica layer is removed from the surface of the particles, it is formed according to the reaction (5), [SiO₄]⁴⁻ units and hydrogen gas (Huang and et.al [11]). in the subsequent hydrolysis and condensation reactions, siloxane groups are formed, which help to stabilize the cell [26].



So it is clear that in an acid environment, Si could better react with N₂ gas. It has already been established that there is a thin film of SiO₂ on the surface of Si particles that prevents the nitrogen in the furnace atmosphere from passing through and reaching the silicon particles' surface. This thin layer reduces the capacity of Si particles to react. An acid environment removes this layer from Si particles' surface and therefore, improves their reaction capability. Thus, it was concluded that the preparation of sol gives a better result in the acid environment compared to the alkaloid environment. Consequently, the other samples were prepared in acid environments.

3.2. Effect of sintering aid

A review of the literature [27,28] shows that sintering is a process under influence of various parameters e.g. the properties of the initial silicon powder, sintering aid, and processing. As a result, the preparation of sintered reaction-bonded silicon nitride ceramic bodies requires a thorough investigation of the parameters affecting the sintering reaction process. Silicon melts around 1412°C, and since the chemical reaction between nitrogen and silicon is exothermic, releasing 759Kj/mol, the applied heat differs from the bodies' temperature. Therefore, the nominal temperature of the furnace is 1350, but due to the release of energy during the reaction of silicon and nitrogen, the temperature is higher on the surface and inside the parts. Following the formation of the initial layer of silicon nitride, the process of nitridation is achieved as nitrogen proceeds and infiltrates into the silicon body. Since nitrogen infiltration in this layer is very slight, it is possible to apply a proper heating regime with step-wise and controlled heating to ensure smooth progress in the reaction, stop silicon from melting, and reduce the risk of cracking in the initial silicon nitride layer. the silicon nitride bodies with a high percent of covalent bonds in their components have specific properties which make them fit for applications in high temperatures and under special conditions. Therefore, it is not possible to use more sintering aid in their fabrication, because sintering aid components have lower softening temperatures in comparison with the background phase which leads to the change in the properties of the bodies at higher temperatures. This is why it is recommended to find the optimal balance for the composition and ratio

of sintering material so that they play their role as aids, and at the same time, the residual liquid phase does not degrade the qualities obtained under high temperature [29,30].

The sintering aid that are commonly used in silicon nitride ceramic bodies react with the SiO_2 coat that covers Si_3N_4 particles and make up a liquid phase that develops the sintering process. Sintering aid are used to form the liquid phase to pave the way for $\beta\text{-Si}_3\text{N}_4$ phase deposition [31]. Therefore, the kinetics of the sintering process, microstructure, and final properties of the sintered Si_3N_4 is determined by the composition of the liquid phase [24,29]. Among various oxides used as a sintering aid for Si_3N_4 bodies, e.g. MgO , Al_2O_3 , Li_2O , Y_2O_3 , etc., Y_2O_3 is reported to form a refractory secondary phase in grain boundaries and therefore, have fewer effects in reducing properties such as flexural strength, thermal shock resistance, and resistance against oxidation of the bodies under high temperatures [29,32,33,34]. In this system, the eutectic point is 1345°C with mixing ratios of 32% yttria, 22% alumina, and 46% silica [32]. This mixture has a low eutectic temperature, yielding the liquid phase, which is at about 1400°C . Based on the phase diagram, the ratio of alumina to yttria was considered 1:3. This ratio was selected following the favorable properties of the sintering aid reported in previous studies [13,35,36]. Although the XRD peaks represent qualitative data, it is possible to get an estimation of the percentage of the phases formed [Figures 6-8]. Figure 5 shows the XRD of the samples containing sintering aid in samples AYS1, AYS2, and AYS3, residual Si, SiO_2 cristobalite, and $\beta\text{-Si}_3\text{N}_4$ were identified.

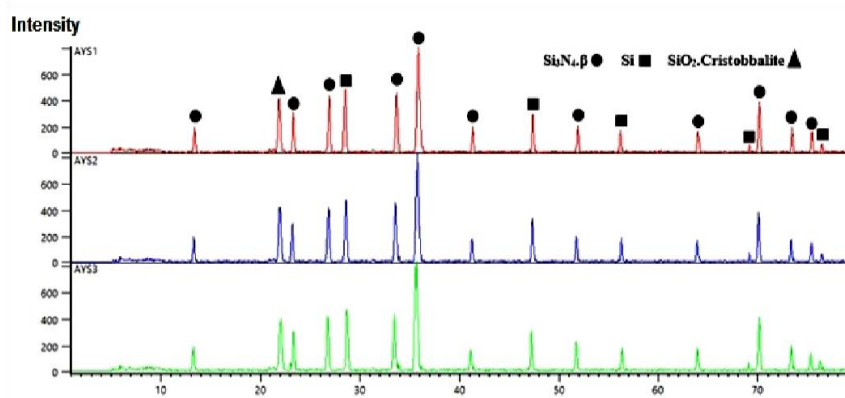


Figure 5. XRD patterns of samples with sintering aid

The main difference between the XRD results of these samples and those without 60A sintering aid (Figure 5) is the increased intensity of the cristobalite peak. Results of $\beta\text{-Si}_3\text{N}_4$ and residual metallic Si phase match the previous findings with good approximation. On the other hand, the difference in the peaks obtained after introducing sintering aid is the increase in the intensity of the cristobalite phase, which can be attributed to adding SiO_2 in the main sample. The percentage of these phases was estimated from the peaks of the X-ray diffraction pattern (Figure 5). Based on the estimated percentages, with an increase in the percent of SiO_2 and a decrease in Al_2O_3 and Y_2O_3 (assuming the ratios are kept constant), the percentage of $\beta\text{-Si}_3\text{N}_4$ dramatically increased and there was some residual Si.

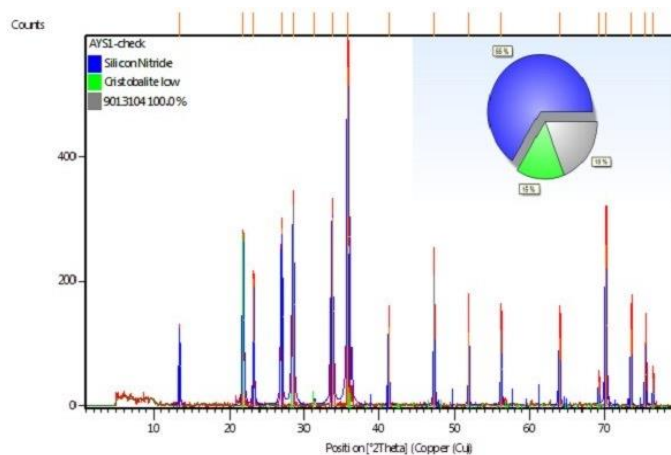


Figure 6. XRD pattern and phase percent diagram of sample AYS1

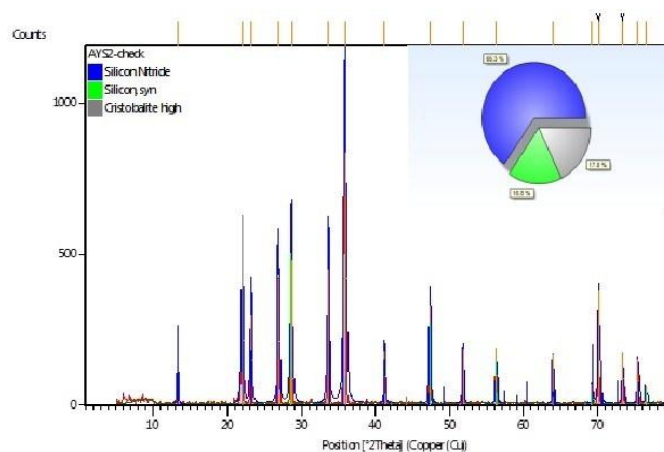


Figure 7. XRD pattern and phase percent diagram of sample AYS2

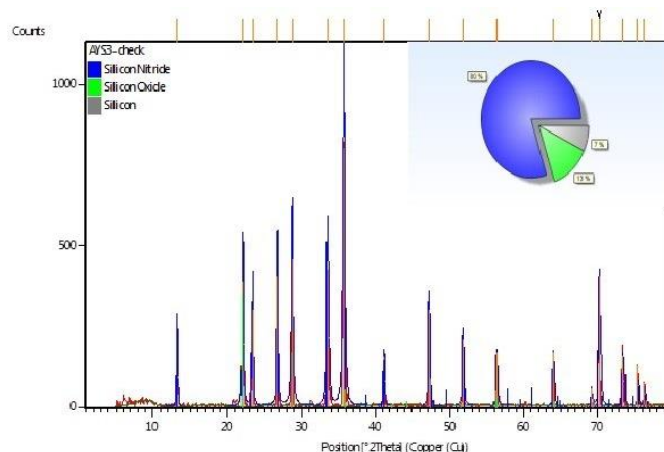


Figure 8. XRD pattern and phase percent diagram of sample AYS3

Nikonam Mofrad et al [24] mentioned that the reaction takes place between nitrogen and silicon in different physical states according to the following equations.



$$\Delta G_0 = -2080 + 0.757T \text{ kJ.mol}^{-1}$$



$$\Delta G_0 = -874 + 0.405T \text{ kJ.mol}^{-1}$$



$$\Delta G_0 = -723 + 0.315T \text{ kJ.mol}^{-1}$$

Previous research has shown that the α - Si_3N_4 is formed due to the reaction of nitrogen with silicon in the gas state. But with the reaction of nitrogen with silicon in solid and liquid states, β - Si_3N_4 is formed. When no additives are used, mainly the alpha phase is formed at a temperature between 1300-1400 °C [37].

3.3. Bulk density

The bulk density of the samples containing additives was analyzed based on the amount of porosity and density of the samples. Results are presented in Table 2. Comparison of the densities of AYS1, AYS2, and

AYS3 samples as shown reveals that the presence of more additives as sintering aid in these samples contributed to the formation of more liquid phase and facilitated the process of sintering, thus samples with higher densities.

Table 2. The bulk density of the samples with sintering aid

Sample	Bulk Density (g.cm ⁻³)	%Porosity
AYS1	2.58	22.6
AYS2	2.57	23.5
AYS3	2.61	22.1

3.5. Microstructure analysis

Figure 9 shows SEM images of the 60 vol% solid load sample prepared in an acid and alkaline suspension environment. The growth of more β - Si_3N_4 grains with elongated rod morphology has happened in an acid environment.

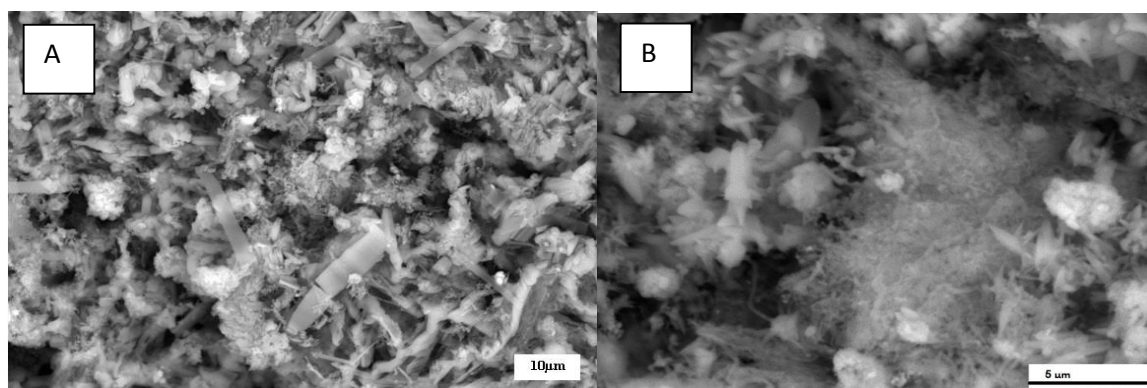
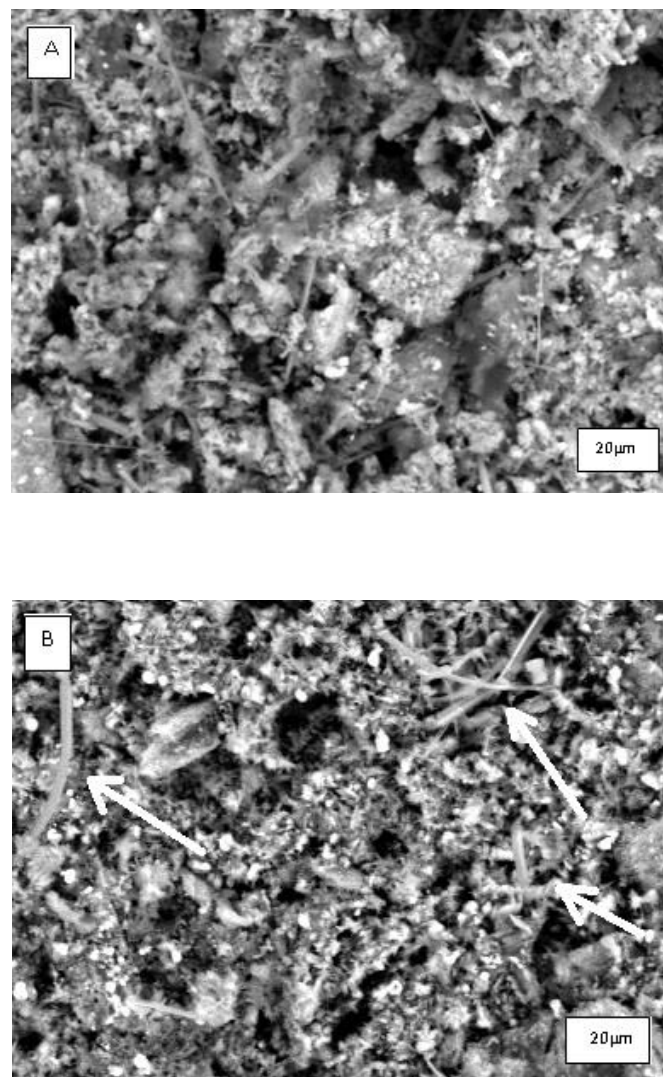


Figure 9. SEM images of the sample prepared in (A) acid (B) alkaline suspension

Figure 10 presents the SEM images of the samples containing sintering aid, where it is clear that adding SiO_2 , Al_2O_3 , and Y_2O_3 sintering compounds improved the formation of elongated $\beta\text{-Si}_3\text{N}_4$ grains, and the presence of the liquid phase greatly enhanced the development of these particles. Based on the XRD results, the $\beta\text{-Si}_3\text{N}_4$ has been formed, but it seems that due to the short time or low nitriding temperature, β grains have little growth in the form of rods. Therefore, the use of sintering aid to form the liquid phase and create $\beta\text{-Si}_3\text{N}_4$ [24]. In the comparison of SEM images and XRD results of samples with sintering aid and samples without additives, it is clear that with the use of sintering aid, the formation of $\beta\text{-Si}_3\text{N}_4$ has increased, and if there is a soaking time at the highest temperature of the process, probably the rod like grains will be growthed.



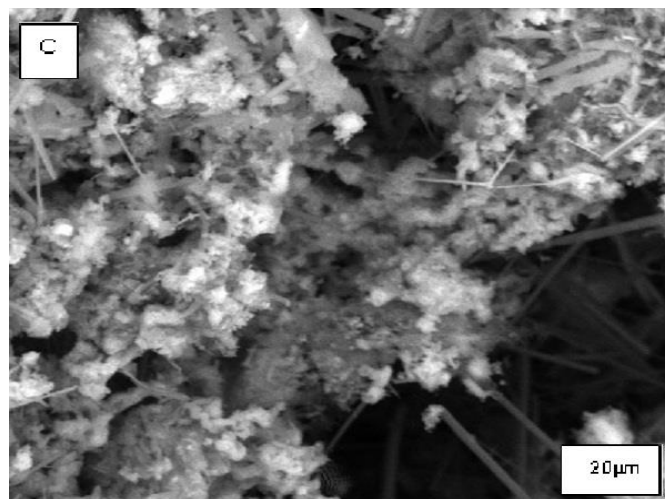


Figure 10. SEM images of the (A) AYS1, (B) AYS2, (C) AYS3 samples containing SiO_2 , Al_2O_3 , and Y_2O_3 sintering aid compounds.

4. Conclusion

The present study aimed to manufacture porous Si_3N_4 ceramic through gel-casting of Si powder. The effects of monomer pH and amount of sintering aid were investigated. Al_2O_3 , Y_2O_3 , and SiO_2 powders (as sintering aid) and Si (as the main powder) were added to obtain a slurry with a solid loading of 60wt%. Results of XRD analysis showed that the final phase in all samples was metallic Si and $\beta\text{-Si}_3\text{N}_4$ along with some percentages of cristobalite. Analysis of the effects of pH on the final phase of the samples made that preparation of the premix in an acid environment leads to an increase in the reactivity of Si with N_2 and relatively more Si_3N_4 is formed in comparison with the alkaline environment, and the slurry prepared in the acidic environment reacted more effectively with N_2 atmosphere. Regarding the effect of sintering aid on the formation of the final phase, the findings suggested that increasing the amount of SiO_2 and reducing Al_2O_3 and Y_2O_3 resulted in more $\beta\text{-Si}_3\text{N}_4$ (from 66% to 80%) and a decrease in the Si metal (from 18% to 7%).

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