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Fabrication and Characterization of Porous Silicon Nitride Bodies through Starch Consolidation Casting and Pressureless Sintering

M. Haghshenas, S. M. Mirkazemi *, F. Golestanifard

Iran University of Science and Technology (IUST), Materials and Metallurgical Engineering

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ABSTRACT

Porous Si_3N_4 ceramics were prepared by a novel colloidal method called starch consolidation casting. In this method, starch plays both pore-forming and consolidating roles. The effect of starch content on the viscosity of Si_3N_4/starch slurry was investigated in this research. Rotational Rheometer was used to study the rheological behavior of Si_3N_4/starch slurry. Green samples with 5 to 10MPa flexural strength were shaped by casting slurries in a nonporous mold and held at 80°C for 120min. Afterward the samples burned-out and sintered at 1650°C for 4h in an air furnace under a nitride powder bed condition. Thermal behavior, phase evolution, and microstructure of sintered samples were characterized through Thermogravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscope (SEM). The XRD results showed that $\beta - Si_3N_4$ was the main phase in the sintered samples. The $\beta - Si_3N_4$ phase content was as much as 90wt% in the sintered samples. Finally, a porous silicon nitride sample was successfully produced with 44 vol% open porosity and Flexural strength of 108.9MPa through the starch consolidation casting method.

1. INTRODUCTION

Silicon Nitride has got great attention in the past few years because of its excellent mechanical and thermo-mechanical properties [1]. Porous Silicon Nitride bodies are more attractive due to their high strength to weight ratio, permeability, and low dielectric constant in applications such as filters, catalyst carriers, bioreactors, wave transparent pieces, etc., especially at high temperatures [2, 3]. Some methods have been applied to produce high strength porous silicon nitride bodies a few of which that contain partial sintering and carbothermal nitridation, and addition of fugitive materials have reached flexural strength more than 150MPa in presence of about 50vol% open porosity [4-7]. However, most of these methods are not able to form a complex near-net-shape body. A simple near-net-shape method for shaping the porous Si_3N_4 ceramics is gel-casting. In common gel-casting method, an organic monomer system is used to shape a rigid green body through gelation step [8]. There are several problems with using these monomer systems according to their reactive and toxic nature as well as their high cost. Alternatives for the synthetic monomer systems in gel-casting are native polymers such as agarose, gelatin, and starch [9]. The Starch Consolidation Casting (SCC) is a novel colloidal method for shaping ceramic bodies using starches as a pore-forming and consolidating agent simultaneously [10]. In recent years, researchers have used SCC to fabricate porous oxide ceramics such as alumina [10-13], cordierite [14], silica [15], and titania [16]. Moreover, Xiao-Jian et al. applied this method for shaping porous SiC ceramics [17]. Although some people have examined the fabrication of porous silicon nitride ceramics through starch addition as a pore-forming agent [4, 18], none of them used colloidal SCC method for this material, yet. In this research, the SCC method has been employed to shape porous samples from silicon nitride starting powder. Initially, the effect of starch addition was investigated on the viscosity of Si_3N_4 aqueous slurry. After shaping, the flexural strength of green bodies was measured. Finally, burning-out and pressureless sintering process was carried out, and the density, final microstructure, flexural strength, and phase transformation of samples were characterized.

*Corresponding Author Email: mirkazemi@iust.ac.ir (S.M. Mirkazemi)

2. MATERIALS AND METHODS

2.1. Raw Materials

A commercial pure silicon nitride powder (The Si_3N_4 powder, d_{50} = 0.4 μm, purity > 98%; Hangzhou) was used in this research. Table 1 shows the chemical analysis and average particle size (d_{50}) of the starting powder. The surface of the starting powder was partially oxidized at 800°C for 2h in an air atmosphere to improve the dispersion of the starting powder in aqueous media. Alumina (Fibrona $d_{50} = 0.33\mu m$) and Yttria ($HC - Starck$, $d_{50} = 0.31\mu m$) were used as sintering aids. A dispersant (Dolapix CE64) was added to the slurry to prevent agglomeration of ceramic powders. Native wheat starch (d_{50}=3.5μm) from the food industry was used as the pore-forming/consolidating agent.

TABLE 1. The starting powder of the chemical composition

D_{50} (μm)	Si (wt. %)	Ca (wt.%)	Fe (wt. %)	C (wt. %)	O (wt. %)	α-Si_3N_4 (wt. %)	Si_3N_4 (wt. %)
0.4	0.2	0.02	0.25	0.2	1.2	90	>98

2.2. Slurry Preparation

The mixture powders of 94wt% Si_3N_4, 4.5wt% Y_2O_3, and 1.5wt% Al_2O_3 were added to the solution containing distilled water and 0.4wt% dispersant (based on powders). The total solid loading in all slurries was 40vol%. The slurries were milled for 24h to break down agglomerates. Afterward, 7.5 to 35vol% starch (based on total solid loading) were introduced to the slurries and subsequent mixing was carried out by a magnetic stirrer for an hour.

2.3. Green Body Shaping

Slurries were degassed for 30 min and casted into nonporous plastic molds to shape the green samples. The molds were kept at 80°C for 120min during which the suspension consolidated and a rigid body was formed. Then, the green bodies were demolded and dried for 72h at ambient temperature.

2.4. Binder Burn-out and Sintering

According to TGA analysis of starch powder (Fig. 1), binder burning out was carried out at 600 °C for 1h in an air furnace with a heating rate of 1°C.min^{-1}. The sintering of samples was done according to the thermal regime shown in Fig. 2. All samples held under a nitride powder bed during sintering to prevent active oxidation or thermal decomposition of Si_3N_4. The composition of the bed powder was as much as 66wt% Si_3N_4 and 33wt% BN.

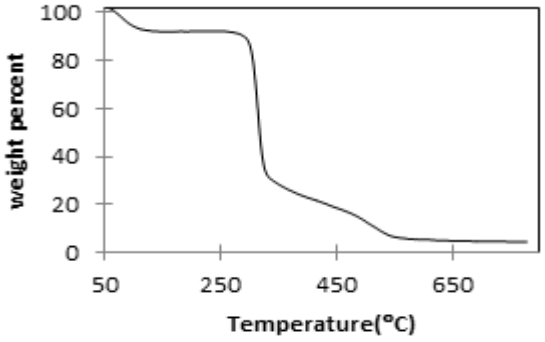

Figure 1. TGA curve of native wheat starch

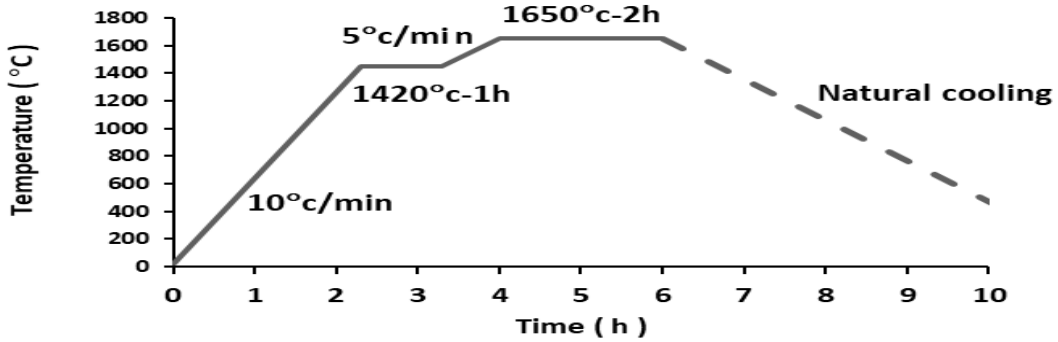

Figure 2. Thermal schedule of Heat treatment of the sintering process

2.5. Measurements

A rotational rheometer (Brookfield LV, DV − ro + PRO) was used to determine the viscosity values of slurries at two constant shear rates of 12.54, 50.57s^{-1}. The bulk density, apparent density, and open porosity of the samples were measured by the Archimedes method using distilled water as a medium according to ASTM C20 standard. The samples were 50×18×10mm in size and were immersed within boiling water for 2h, then, cooled to the ambient temperature and rested for at least 12h before their wet weight collected.

The samples were machined into $45 \times 4 \times 3$mm test bars and polished using a C-BN plate for the mechanical properties measurement. Flexural strengths of the samples were measured according to ASTM-C1161-02C standard by a 3-point bending test machine (SANTAM, STM-20; Iran). The span and crosshead speeds were 40mm and 0.5mm.min^{-1}. The fracture surfaces of the samples were characterized by a scanning electron microscope (SEM; TESCAN, VEGAII; Czech Republic). The phase compositions were identified through X-ray diffraction (XRD; Philips; Netherlands) using Cu $K\alpha$ radiation at 40KV and 100mA. The $\beta - Si_3N_4$ phase content ($\beta\%$, wt%) was determined using XRD peak intensities by Equation 1 [20]:

$$\beta\% = \frac{I_{\beta\,(101)} + I_{\beta\,(210)}}{[\,I_{\alpha\,(102)} + I_{\alpha\,(210)}\,] + [\,I_{\beta\,(101)} + I_{\beta\,(210)}\,]} \times 100 \qquad (1)$$

Where $I_{\alpha(102)}$ and $I_{\alpha(210)}$ are the intensities of (102) and (210) diffraction planes of $\alpha - Si_3N_4$, and $I_{\beta(101)}$ and $I_{\beta(210)}$ denote the intensities of (101) and (210) planes of $\beta - Si_3N_4$, respectively.

3. RESULTS AND DISCUSSION

3.1. Effect of Starch Content on Viscosity

The viscosity of a ceramic/starch slip should be low enough to permit adequate mold filling without entrapping air, but at the same time, they have to be high enough to avoid the critical segregation phenomena at rest before consolidation takes place [10]. One of the crucial steps in gel casting is the preparation of a suitable powder suspension in terms of its rheological properties, solid loading, homogeneity, and stability. High solids loading and low viscosity are important to avoid casting issues that are correlated to the physical and mechanical properties of the green body. The rheological properties of the suspensions are mainly influenced by solid loading and gelling agent content and generally show a pseudoplastic behavior (Fig. 3a). However, a critical value of solid loading can be defined, which determines the shift from a shear thinning behavior to a shear-thickening one (Fig. 3b). Several authors consider the value of 1Pa.s determined for shear rates between 10 s^{-1} and 100 s^{-1} to be the limit of apparent viscosity that allows good de-airing and casting processes to take place [11-19].

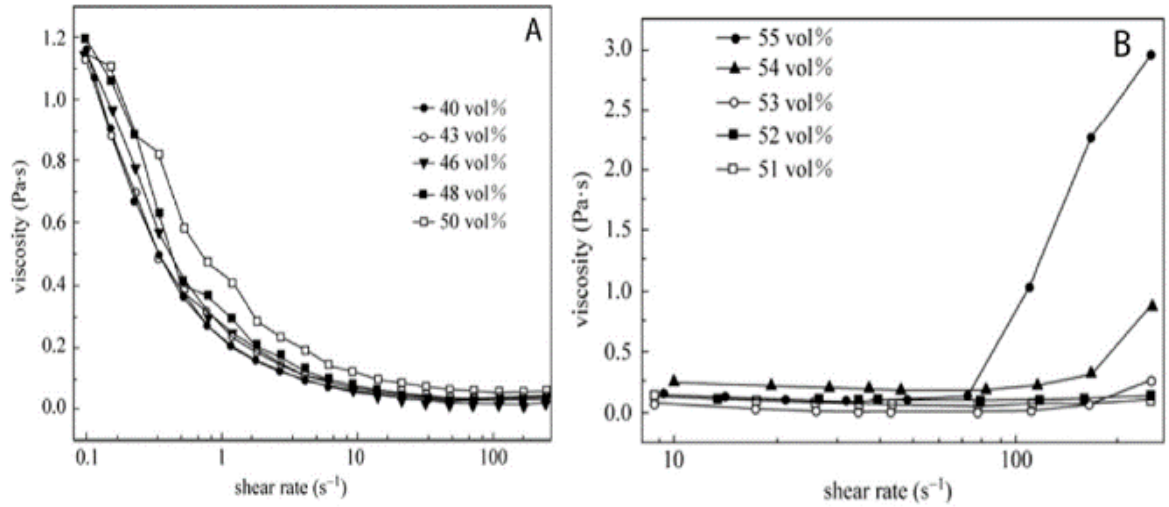

Figure 3. Rheological behavior of aqueous alumina suspensions with different solid loadings (a) from 40 to 50vol% and (b) from 51 to 55vol%

Figure 4 shows the viscosity of the slurry against starch content in two different shear rates. As can be observed, all slurries have viscosities lower than 100mPa.s, which is low enough for casting. Increasing the starch content up to 20vol% lowers the viscosity, but the viscosity becomes higher when the starch content reaches more than 20vol%, which is consistent with the viscosity measurements of the alumina-starch slurry by

Lyckfeldt and Ferreira [10]. According to their explanation, the viscosity of the slurry changes by introducing starch for three reasons. First, the total exposed surface area of the solids decreases when large granules of starch substitute fine particles of ceramic powders, so the viscosity of slurry decreases. Second, reaching to an optimum particle packing according to double-sized particles lowers the viscosity up to certain starch content. Third, the water uptake by starch granules increases the real solid loading of the slurry as well as the viscosity. The first two mechanisms dominate at lower starch content and the other mechanism dominates at higher starch content.

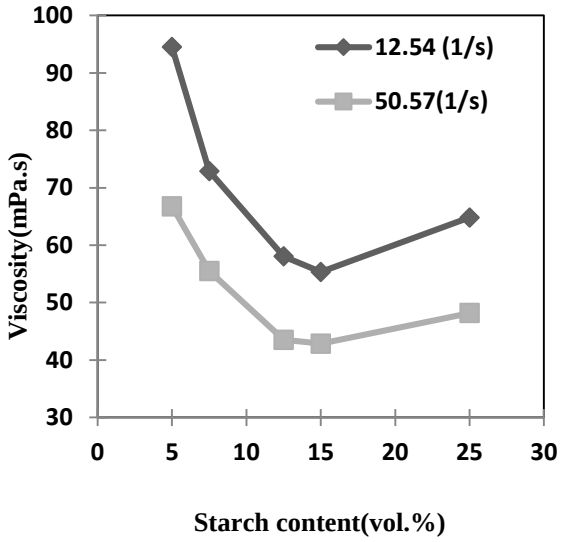

Figure 4. Effect of starch content (based on the total solid loading) on the viscosity of Si_3N_4/starch aqueous slurry

3.2. Green Strength

Fig. 5 shows the flexural strength of green samples. All samples had green strength between 5 to 10MPa. Although these values are lower than the similar samples produced via common gel-casting method [26], they are sufficient for demolding and even green machining. This makes the SCC method needless to machining hard sintered samples. The green strength of samples increases with increasing the starch content due to a more compacted gel network, respectively.

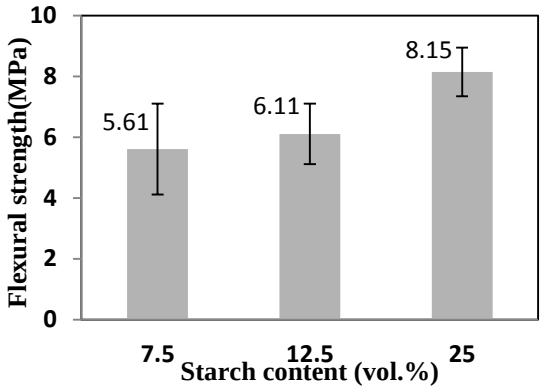

Figure 5. Flexural strength of green samples with different starch contents

3.3. Density and Strength of the Sintered Samples

Table 2 shows the bulk and apparent density, open porosity, and flexural strength of sintered samples. Total solid loading in all samples was 40vol%. As starch content increases, the open porosity of sintered samples increases and the bulk density decreases, respectively. The maximum bulk density is as much as 1.95g.cm^{-3} in the sample containing 7.5vol% starch and its minimum value is as much as 1.60g.cm^{-3}. Forming green bodies with lower than 7.5vol% of starch content was not possible because of their high water to starch ratio. Therefore, reaching bodies with higher density or lower porosity is not possible through this method. According to the decrease of open porosity, it is reasonable that the flexural strength of samples increases as starch content decreases. The flexural strength of samples produced in this research is comparable with samples produced through other methods [4-7].

TABLE 2. Physical and mechanical properties of sintered samples

Sample number	Starch content (vol. %)	Open porosity (vol. %)	Bulk density (g/cm^3)	Flexural strength (MPa)
1	7.5	38.3	1.95	105.5
2	12.5	44.0	1.80	108.9
3	25	46.5	1.74	70.1
4	35	47.8	1.60	-

3.4. Phase Transformation and Microstructure

Fig. 6 shows the X-ray diffraction patterns of starting powder and sintered sample. These patterns show that β-Si_3N_4 is the main phase in the sintered sample. Determination of $\beta - Si_3N_4$ phase content in starting powder and sintered sample shows that α-β transformation is almost done in 4h at 1650°C. β phase contents were 10 and 92wt % for starting powder and sintered sample. Further discussion is given in the previous article [27].

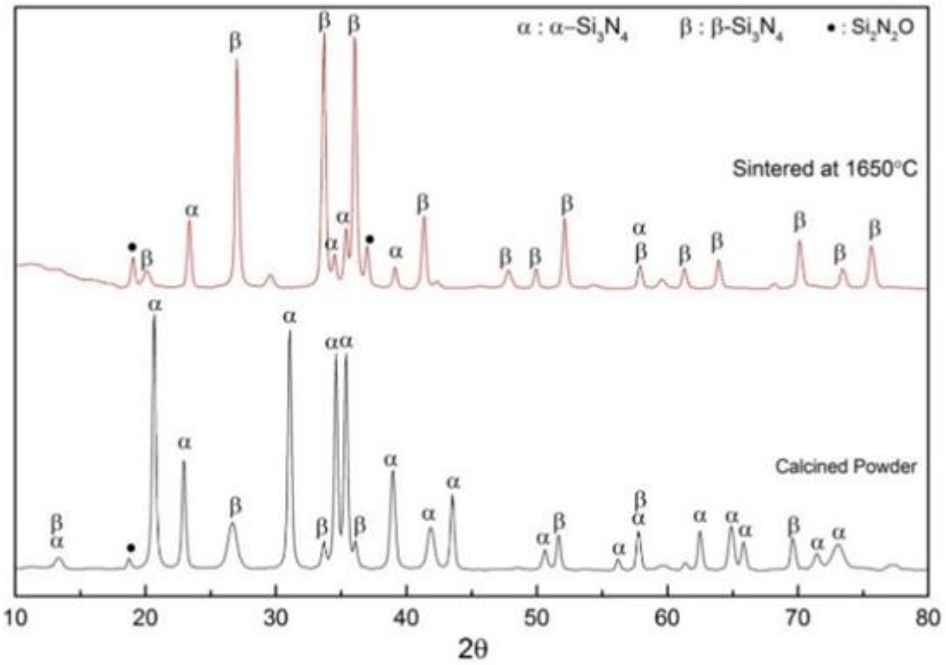

Figure 6. XRD patterns of starting powder and sintered sample

Fig. 7 shows the SEM micrograph of initial starch granules and fracture surface of a porous sample after sintering. The uniform spherical pores in this image are relevant to the spherical shape of starch initial granules. The average diameter of these pores is about 8μm, which is considered 2 times larger than the average diameter of the starch starting granules. The reason for this size difference between pores and starch granules is the starch swelling phenomena during the consolidation process at 80°C. The elongated β-Si_3N_4 grains are visible in higher magnification image of the sintered sample fracture surface. The phase transformation from α-Si_3N_4 to β-Si_3N_4 and the anisotropic growth of grains causes a three-dimensional interlocking microstructure of elongated β-Si_3N_4 grains, which leads to improved mechanical properties. Hence, the high strength of sintered porous Si_3N_4 samples is reasonable.

4. CONCLUSION

The effect of starch content was investigated on the viscosity of Si_3N_4/starch slurry. Increasing starch content up to 20vol% decreases the viscosity of the slurry, but further starch addition causes an increase in viscosity. Porous Si_3N_4 ceramics with 44vol% open porosity were prepared by starch consolidation casting and pressureless sintering. A three-dimensional interlocking microstructure of elongated β-Si_3N_4 grains was formed due to the phase transformation from α-Si_3N_4 to β-Si_3N_4 and the anisotropic growth of grains, which lead to improved mechanical properties. The flexural strength of ceramics ranged 70.1-108.9MPa. Therefore, SCC is considered as an efficient way to prepare high performance porous Si_3N_4 ceramics.

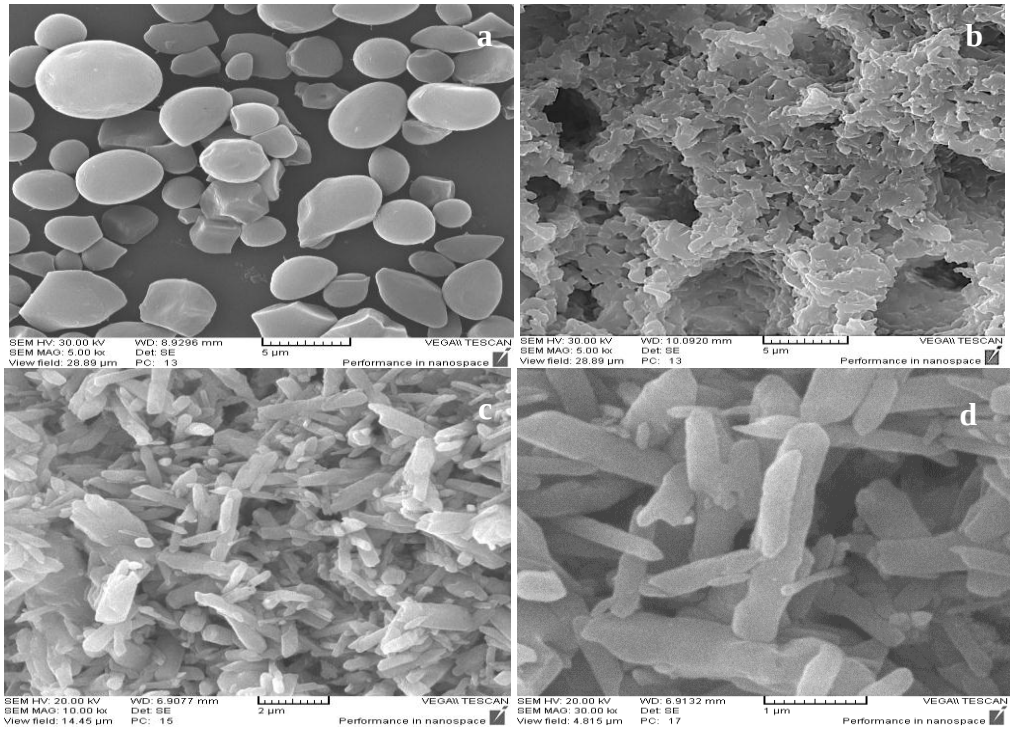

Figure 7. SEM micrograph (a) initial Si_3N_4 powder and starch granules (b) porous Si_3N_4 sample sintered at 1650°C for 2h (c) porous Si_3N_4 sample sintered at 1650°C for 4h (mag. X 10000) (d) porous Si_3N_4 sample sintered at 1650°C for 4h (mag. 30000 X)

5. ACKNOWLEDGMENT

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6. REFERENCES

1. Hampshire, S., "Silicon nitride ceramics – review of structure , processing and properties", ***Journal of Achievements in Materials and Manufacturing Engineering***, vol. 24, No. 1, (2007), 43–50.
2. Yang, J.F., Deng, Z.Y., Ohji, T., "Fabrication and characterisation of porous silicon nitride ceramics using Yb_2O_3 as sintering additive", ***Journal of the European Ceramic Society***, Vol. 23, No. 2, (2003), 371-378.
3. Yang, J., Yang, J.F., Shan, S.Y., Gao, J.Q., Ohji, T., "Effect of sintering additives on microstructure and mechanical properties of porous silicon nitride ceramics", ***Journal of the American Ceramic Society***, Vol. 89, No. 12, (2006), 3843-3845.
4. Kalemtas, A., Topates, G., Özcoban, H., Mandal, H., Kara, F., Janssen, R., "Mechanical characterization of highly porous β-Si_3N_4 ceramics fabricated via partial sintering & starch addition", ***Journal of the European Ceramic Society***, Vol. 33, No. 9, (2013), 1507-1515.
5. Li, X., Zhang, L., Yin, X., "Fabrication and properties of porous Si_3N_4 ceramic with high porosity", ***Journal of Materials Science & Technology***, Vol. 28, No. 12, (2012), 1151-1156.
6. Shan, S.Y., Yang, J.F., Gao, J.Q., Zhang, W.H., Jin, Z.H., Janssen, R., Ohji, T., "Porous silicon nitride ceramics prepared by reduction–nitridation of silica", ***Journal of the American Ceramic Society***, Vol. 88, No. 9, (2005), 2594-2596.
7. Li, Y., Chen, F., Li, L., Zhang, W., Yu, H., Shan, Y., Shen, Q., Jiang, H., "Gas pressure sintering of arbitrary porous silicon nitride ceramics with high mechanical strength", ***Journal of the American Ceramic Society***, Vol. 93, No. 6, (2010), 1565-1568.
8. Li, L., Wang, H., Su, S., "Porous Si_3N_4 ceramics prepared by TBA-based gel-casting", ***Journal of Materials Science & Technology***, Vol. 31, No. 3, (2015), 295-299.
9. Yang, J., Yu, J., Huang, Y., "Recent developments in gelcasting of ceramics", ***Journal of the European Ceramic Society***, Vol. 31, No. 14, (2011), 2569-2591.
10. Lyckfeldt, O., Ferreira, M. F., "Processing of Porous Ceramics by 'Starch Consolidation", ***Journal of the European Ceramic Society***, Vol. 18, No. 2, (1998), 131–140.
11. Huang, Y., Yang, J., "Generation, development, inheritance, and control of the defects during the transformation from suspension to green body" in ***Novel Colloidal Forming of Ceramics***, Springer, Tsinghua University Press, Beijing and Springer-Verlag Berlin Heidelberg, (2010), pp. 129–210.
12. Ha, C.G., Jung, Y.G., Kim, J.W., Jo, C.Y., Paik, U., "Effect of particle size on gelcasting process and green properties in alumina", ***Materials Science and Engineering: A***, Vol. 337, No. 1-2, (2002), 212-221.
13. Yang, J., Xie, Z., Tang, Q., Huang, Y., "studies on rheological behaviour and gelcasting of alpha-Al_2O_3 suspension", ***Journal of the Chinese Ceramic Society***, Vol. 26, No. 1, (1998), 41-46.
14. Chen, L., Song, X.L., Ye, J.D., Li, B., "Colloidal in-situ consolidation forming of Al_2O_3 ceramics using modified starch", In ***Key Engineering Materials,*** Vol. 280, (2005), pp. 1027-1032, Trans Tech Publications.

15. Tulliani, J.M., Lombardi, M., Palmero, P., Fornabaio, M., Gibson, L.J., "Development and mechanical characterization of novel ceramic foams fabricated by gel-casting", ***Journal of the European Ceramic Society***, Vol. 33, No. 9, (2013), 1567-1576.
16. Adolfsson, E., "Gelcasting of zirconia using agarose", ***Journal of the American Ceramic Society***, Vol. 89, (2006), 1897–1902.
17. Xu, J., Gan, K., Yang, M., Qu, Y., Wu, J., Yang, J., "Direct coagulation casting of yttria-stabilized zirconia using magnesium citrate and glycerol diacetate", ***Ceramics International***, Vol. 41, No. 4, (2015), 5772-5778
18. Khattab, R.M., Wahsh, M.M.S., Khalil, N.M., "Preparation and characterization of porous alumina ceramics through starch consolidation casting technique", ***Ceramics International***, Vol. 38, No. 6, (2012), 4723-4728.
19. Chandradass, J., Kim, K.H., sik Bae, D., Prasad, K., Balachandar, G., Divya, S.A., Balasubramanian, M., "Starch consolidation of alumina: Fabrication and mechanical properties", ***Journal of the European Ceramic Society***, Vol. 29, No. 11, (2009), 2219-2224.
20. Gregorová, E., Pabst, W., "Process control and optimized preparation of porous alumina ceramics by starch consolidation casting", ***Journal of the European Ceramic Society***, Vol. 31, No. 12, (2011), 2073-2081.
21. Alves, H.M., Tarı, G., Fonseca, A.T., Ferreira, J.M.F., "Processing of porous cordierite bodies by starch consolidation", ***Materials Research Bulletin***, Vol. 33, No. 10, (1998), 1439-1448.
22. Xiao-jiana, M.A.O., Shi-weia, W.A.N.G., Shun-zoa, S.H.I.M.A.I., "Preparation of porous silica ceramics with low dielectric constant", ***Chinese Journal of Aeronautic***, Vol. 19, No. S1, (2006), 239-243.
23. Mahata, S., Nandi, M.M., Mondal, B., "Preparation of high solid loading titania suspension in gelcasting using modified boiling rice extract (MBRE) as binder", ***Ceramics International***, Vol. 38, No. 2, (2012), 909-918.
24. Marins, E. M., de Lucena, E.F., de Paula Santos, F., de Campos, E., Melo, F.C.L., Netto, D.B., "Commercial starch consolidation technique for shaping silicon carbide ceramics", in ***17th International Congress of Mechanical Engineering, Sao-Paoulo, SP, eleasar@ lcp. inpe. br.***, (2003).
25. Díaz, A., Hampshire, S., "Characterisation of porous silicon nitride materials produced with starch", ***Journal of the European Ceramic Society***, Vol. 24, No. 2, (2004), 413-419.
26. Yu, J., Wang, H., Zeng, H., Zhang, J., "Effect of monomer content on physical properties of silicon nitride ceramic green body prepared by gelcasting", ***Ceramics International***, Vol. 35, No. 3, (2009), 1039-1044.
27. Parsi, A., Golestani-Fard, F., Mirkazemi, S.M., "The effect of gelcasting parameters on microstructural optimization of porous Si3N4 ceramics", **Ceramics International**, Vol. 45, No. 8, (2019), 9719-9725.