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ARTICLE

Silicon nitride porous ceramics prepared by sacrificial method*

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Abstract

In this work, a comprehensive study was conducted to examine the impact of ammonium bicarbonate (NH_4HCO_3) content, a porogenic agent, on the development of the microstructure, compressive strength, and Young's modulus of the porous silicon nitride ceramics using the sacrificial method. The porous ceramics were obtained by pressureless sintering at 1650 °C and characterized by scanning electron microscopy and X-ray diffraction. The findings demonstrated that all samples developed a microstructure with β-Si_3N_4 grains, but α-Si_3N_4 and wollastonite were also identified. Moreover, grains with a high aspect ratio are predominant in the pore inner structure. The pore morphology was changed from spherical to irregular when the highest NH_4HCO_3 content was used. Under this condition, interconnected pores were also present. The values of compressive strength and Young's modulus decreased with increasing porogen content. The reduction was more pronounced for the ceramic prepared with the highest NH_4HCO_3 content.
Keywords: silicon nitride, porous ceramics, sacrificial method, ammonium bicarbonate.

INTRODUCTION

Porous silicon nitride (Si_3N_4) ceramics have been considered an important material to be used for a wide range of applications such as casting industry, filtration systems, aerospace wave-transmitting materials, catalyst supports, biomedical applications and thermal insulation [1, 2], owing to their great mechanical, thermal and biological behavior which includes lightweight, low thermal expansion coefficient, excellent, thermal stability, relatively high compressive strength, biocompatibility and dielectric properties, as well [1, 3]. Different routes can be used to produce porous ceramics, such as partial sintering, replica method, direct foaming method, sacrificial template method, and additive manufacturing. However, although the microstructure and properties of the porous ceramics are strongly influenced by the technique, the sacrificial method is one of the most used since it is the simplest route for obtaining porous structures [1, 3-7].

The sacrificial template method typically involves creating a biphasic composite characterized by a sacrificial phase homogeneously dispersed in a ceramic matrix. The sacrificial phase is later removed through specific heat treatment, leaving pores within the microstructure with sizes and shapes like the particles of the chosen porogenic agent [5, 6, 8-12]. This method is particularly effective for producing ceramics with macroporosity (d > 50 nm), but it also allows obtaining open-cell or closed-cell structures, according to the kind and amount of the used porogenic agent. While the open-cell structures, defined by the presence of interconnected pores, are an important characteristic for applications requiring fluid transport, such as scaffolds for tissue engineering, a ceramic matrix containing predominantly isolated pores is suitable for applications such as thermal insulation [2, 13]. Porous silicon nitride ceramics with isolated pores could be produced by the sacrificial method with starch as a porogenic agent [11]. The authors found porosity of 5-35 % and flexural strength of 200-1800 MPa and attributed these values to the good results of mechanical properties of the interlocked microstructure due to the in-situ formation of elongated β-Si_3N_4 grains. Using polymethyl methacrylate (PMMA) as a porogenic agent, porous SiC-Si_3N_4 ceramics [11] were also prepared by the same method after sintering at 1450 °C. The ceramics presented α-SiC, α-Si_3N_4, and β-Si_3N_4 as main crystalline phases and porosity between 36 and 64 %, depending on the used PMMA amount. Combined routes can also be used to optimize the final microstructure of the porous component. For instance, the foaming method with the addition of hydrophobic epoxy resin particles as a porogenic agent was used to obtain porous silicon nitride [14]. Samples presented porosity of 71-77% and interconnected pores with two size ranges related to the foaming (50-200 μm) and porogenic agent (1-2 μm). In addition, researchers [12] prepared porous Si_3N_4 ceramics by aqueous gel casting using Si_3N_4 poly-hollow microspheres as a porogenic agent. After the heat treatments, the authors observed that the Si_3N_4 poly-hollow microspheres could create isolated pores with an uniform distribution, promoting porosity between 34 and 43%, compressive strength higher than 90 MPa, and fracture

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toughness of up to 3.0 MPa.m$^{1/2}$.

There are various kinds of porogenic agents, including natural and synthetic materials, such as commercially ground coffee, waxes, seeds, starches, salts (ammonium bicarbonate, sodium carboxymethylcellulose), and synthetic polymers (polymethyl methacrylate) [5, 6, 8-12]. In this paper, porous silicon nitride ceramics were fabricated by the sacrificial method using NH_4HCO_3 to promote pore formation. The porogenic agent was selected considering that NH_4HCO_3 decomposes in NH_3, H_2O, and CO_2 and leaves spaces within the ceramic matrix, favoring the formation of a three-dimensional pore structure [10]. Hence, the influence of NH_4HCO_3 contents on the phase composition, porosity, microstructure, and mechanical properties of the porous ceramics sintered at 1650 ^oC for 1 h were investigated.

EXPERIMENTAL

As starting materials, commercial α-Si_3N_4 powder (95% purity, UBE, Japan), SiO_2 (99.9% purity, Sigma-Aldrich, Germany), $CaCO_3$ (99% purity, Merck, Germany), and NH_4HCO_3 (99.55% purity, CRQ Produtos Químicos, Brazil) were used. NH_4HCO_3 was used as a porogenic agent. The powders were initially dosed to form a composition with 80 wt.% Si_3N_4, 10 wt.% SiO_2 and 10 wt.% CaO, coded as SNSC [15,16]. The powder mixture was ground in a ball mill for 24 hours using isopropyl alcohol as the liquid medium. Following the grinding process, the powder composition was dried in a rota evaporator at 70 °C. To obtain the porous bodies, SNSC powders were mixed with different NH_4HCO_3 contents using an orbital mill (WAB T2C) for 3 h at 27 rpm, resulting in the compositions shown in Table I. After milling, the powder mixtures were compacted by uniaxial pressing (50 MPa) to obtain cylinders (length = 16.5 mm, diameter = 10 mm) and bars (length = 60 mm, width = 6 mm, height = 5.5 mm), which were calcined in a tubular furnace (Lindberg/Blue STF54454C) at 300 °C for 1 h, with a heating rate of 1°C/min. Differential thermal analysis (DTA, Netzsch 404F3) was performed under synthetic air to investigate the decomposition temperature of the NH_4HCO_3 powder. Finally, the green bodies were soaked in a powder bed of silicon nitride to be sintered at 1650 ^oC for 1 h using a graphite resistance furnace (Thermal Technology Inc. 1000-4560-FP20) in a high purity nitrogen atmosphere.

Table I – Compositions of the studied samples.

Samples	SNSC (wt.%)	NH_4HCO_3 (wt.%)
SNSC 50	66	34
SNSC 60	57	43
SNSC 70	46	54
SNSC 80	33	67

The apparent density and porosity were measured following Archimedes' principle, while the relative density was calculated considering the theoretical density of 3.13 g/cm^3, determined by the rule of mixtures. Phase analysis was performed by X-ray diffraction (Cu-Kα radiation source operated at 40 kV and 40 μÅ) in a range from 10 to 90^o (2θ) with the step of 0.02^o (2θ) and 5s/pass (XRD, Brucker D8). The morphology and pore structures were analyzed with a scanning electron microscope (SEM, Hitachi TM-3000) using the fractured surfaces of the porous sintered samples. The compressive tests were carried out with a loading speed of 0.5 mm/min using a universal material testing machine (Instron 4400). A non-destructive dynamic method (ASTM E 1876-15) [17] was used to determine the Young's modulus. By this method, the resonant frequency of the specimens was measured in flexion mode using the GrindoSonic instrument, model MK5 Industrial, with a frequency range of 20 Hz – 100 kHz. The instrument measures the frequency due to transient natural vibrations emitted by a sample as a result of a mechanical impulse. The flowchart of the experimental procedure is shown in Figure 1.

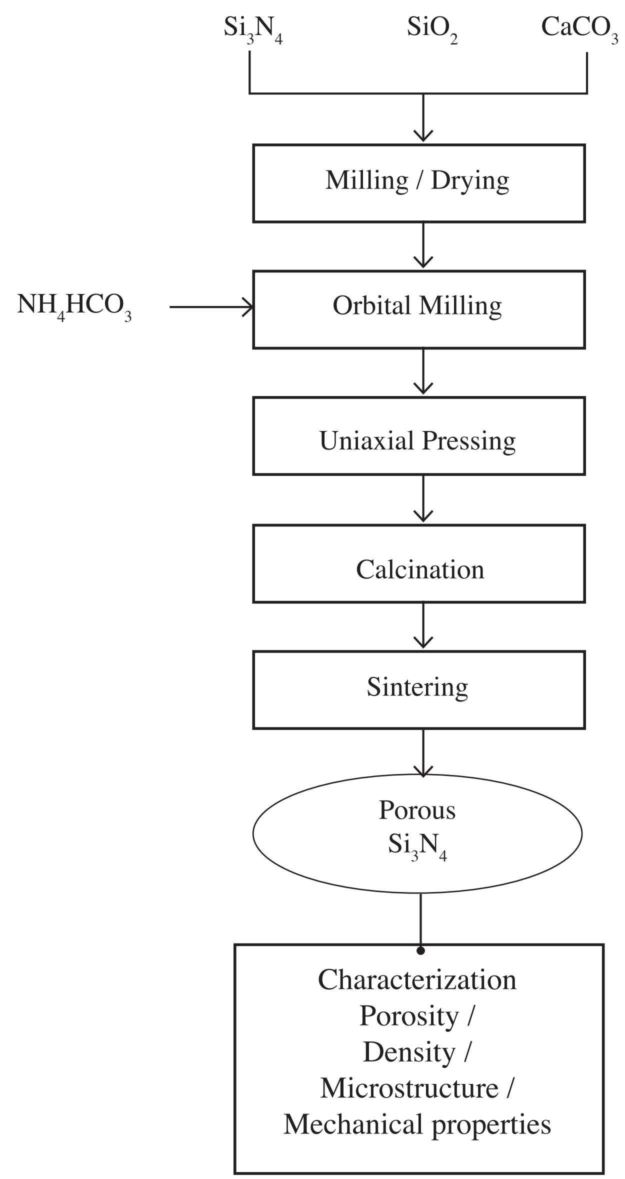

Figure 1: Flowchart of the experimental procedure.

RESULTS AND DISCUSSION

The DTA curve of the commercial NH_4HCO_3 is given in Figure 2. It indicates a thermal event in the temperature range from ~75 to ~275 °C, corresponding to the decomposition of the powder into ammonia, carbon dioxide, and water vapor. From this result, the green bodies were calcined at 300 °C to ensure the total removal of the NH_4HCO_3 added as a porogenic agent.

Figure 3 illustrates the porosity and apparent density of the porous Si_3N_4 ceramics as a function of NH_4HCO_3 content. Porosity increased from ~25 to ~69 % with the higher porogenic agent content, suggesting that NH_4HCO_3 was efficient in producing the porous ceramics. However, it is important to observe that the temperature of 1650°C is significantly low to sinter silicon nitride, which also contributed to the overall porosity due to an incomplete sintering process. It is in good agreement with the XRD results (Figure 4), which show that despite the use of a high concentration of sintering aids (20 wt.%), the transformation from α-Si_3N_4 to β-Si_3N_4 phase was not completed in all samples. Additionally, wollastonite ($CaSiO_3$) was identified as a secondary phase in the ceramics, resulting from the partial crystallization of the liquid phase formed during sintering. Wollastonite as a secondary phase was a significant finding for the studied ceramics since it has suitable properties for some applications of porous materials, such as high thermal stability, bioactivity, and good degradability. Its presence can improve the material performance in applications such as thermal insulation and scaffold for tissue engineering [18].

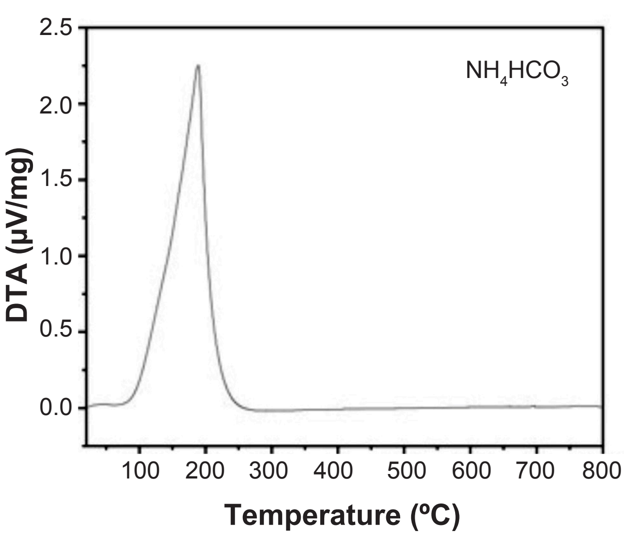

Figure 2: DTA curve of the NH_4HCO_3 powder.

SEM images of the fractured surfaces of porous Si_3N_4 ceramics are presented in Figure 5. The images show that the number of pores increased when the higher porogenic agent was used to produce the ceramics. Also, interconnectivity and change in the pores morphology from spherical to irregular are observed for the SNSC 80 coded sample. This result can be attributed to the increased contact of porogen particles owing to the highest NH_4HCO_3 content in the green body, expanding the application potential of porous

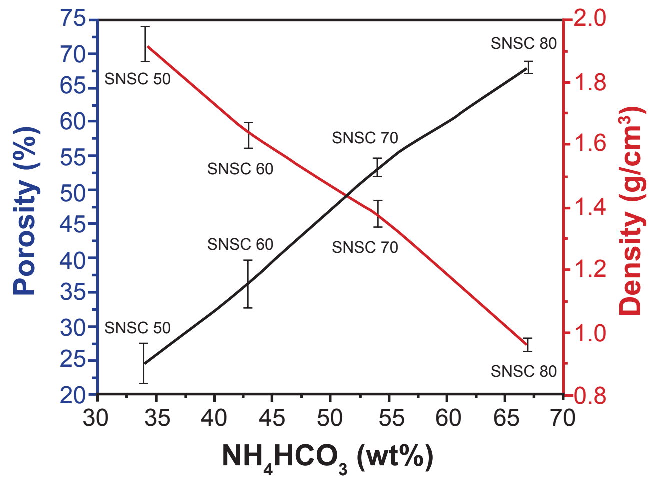

Figure 3: Porosity and apparent density of the porous Si_3N_4 ceramics as a function of the porogenic agent content.

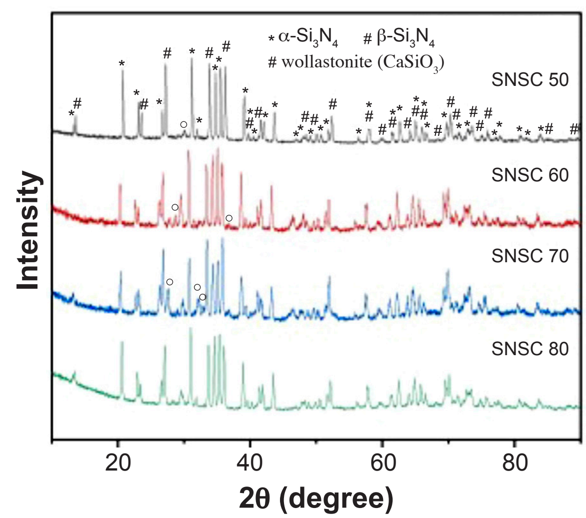

Figure 4: Patterns of X-ray diffraction of the porous Si_3N_4 ceramics.

silicon nitride prepared by the sacrificial method. At higher magnifications, Si_3N_4 grains with low aspect ratios are evident on the pore walls. On the other hand, fibrous Si_3N_4 grains with morphology are predominantly observed from internal pores walls, forming an interlocking microstructure, as the space into the pores reduces the steric hindrance of grain growth [19]. These features are essential for enhancing the mechanical properties of the final ceramics.

Figure 6 presents the results of compression tests conducted on the porous Si_3N_4 ceramics after sintering. Generally, the compressive strength of the samples reduced with increasing porosity, i.e., prepared with higher porogenic agent content. However, the sample produced with the highest porogen content exhibited a drastic reduction in strength. The high porosity, irregular pore morphology, and interconnecting pore network significantly increased the stress concentration points and consequently reduced the compressive strength for SNSC80 (~25 MPa) compared to the SNSC70 (~97 MPa). Higher NH_4HCO_3 content

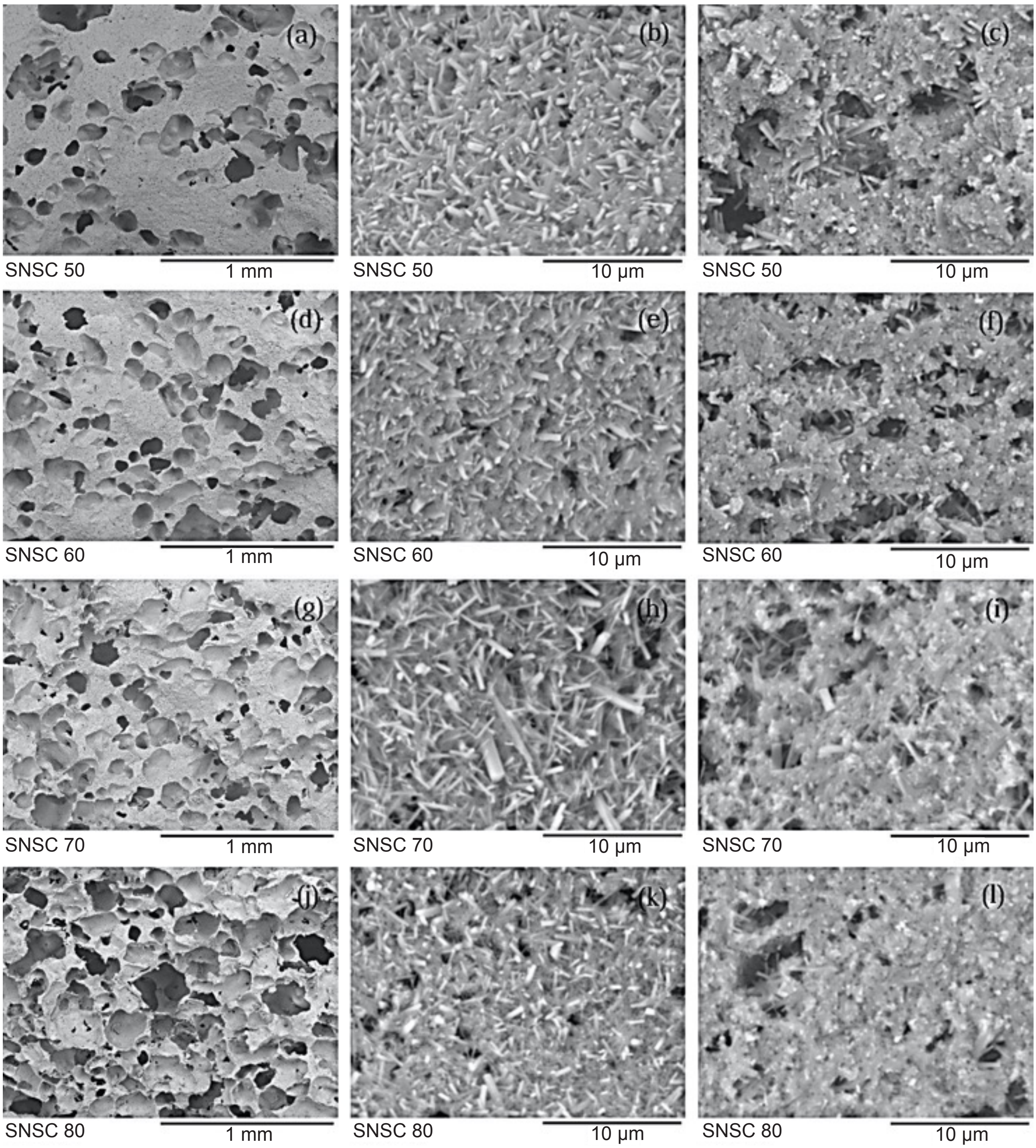

Figure 5: SEM of the sintered porous silicon nitride ceramics. (a) SNSC 50 sample, (d) SNSC 60 sample, (g) SNSC 70 sample, (j) SNSC 80 sample, (b) pore inner structure of SNSC 50 sample, (e) pore inner structure of SNSC 60 sample, (h) pore inner structure of SNSC 70 sample, (k) pore inner structure of SNSC 80 sample, (c) pore wall structure of SNSC 50 sample, (f) pore wall structure of SNSC 60 sample, (i) pore wall structure of SNSC 70 sample and (l) pore wall structure of SNSC 80 sample.

also decreased Young's modulus of the studied materials (Figure 7), but it can be beneficial for some applications. Low Young's moduli are interesting for high-temperature applications to enhance the thermal shock resistance of porous ceramics and reduce stress shielding in biomedical implants [20]. Hence, the low Young's modulus (~19 GPa) comparable to that of cortical bone (7-30 GPa) of the SNSC 80 sample [21, 22], combined with its ~69% porosity, highlights the potential of porous Si_3N_4 ceramics as a possible material for ceramic bone scaffolds manufactured by a relatively simple route.

In summary, the compressive strength and Young's modulus of porous Si_3N_4 ceramics were strongly influenced by the porosity, pores morphology, and interconnectivity.

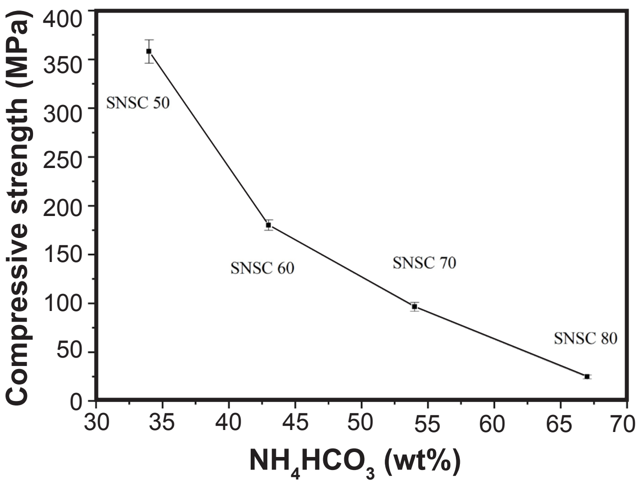

Figure 6: Compressive strength as a function of NH_4HCO_3 content.

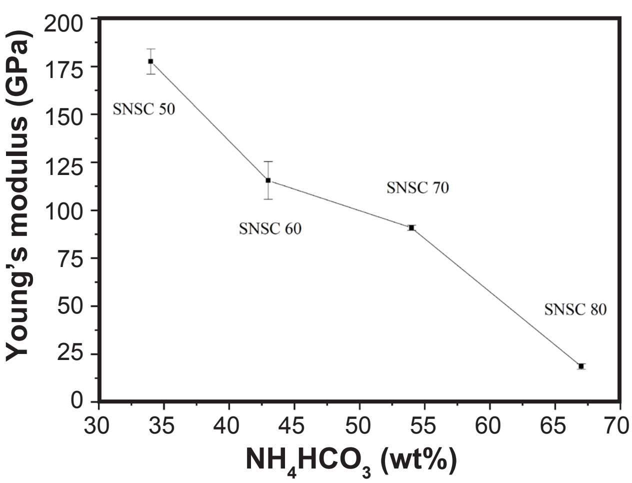

Figure 7: Young's modulus as a function of NH_4HCO_3 content.

As the NH_4HCO_3 content increased from 34 to 67 wt.%, the porosity, compressive strength, and Young's modulus reached approximately 69%, 25 MPa, and 19 GPa, respectively. All samples presented a microstructure with α-Si_3N_4 and β-Si_3N_4 grains dispersed in a secondary phase containing wollastonite. However, fibrous grains were more easily found within the pores. The results indicate that the sacrificial method combined with the used porogen and low temperature sintering are appropriate to produce porous Si_3N_4 ceramics simply and cost-effectively. In addition, by controlling the manufacturing parameters, it is possible to meet the balance between porosity, compressive strength, and Young's modulus required for different applications.

CONCLUSION

Highly porous silicon nitride ceramics were successfully obtained by the sacrificial method using NH_4HCO_3 as a porogenic agent. Samples with different NH_4HCO_3 contents were sintered by sintering at 1650 ºC for 1 hour. Silica and calcia were used as sintering aids with a total concentration of 20 wt.%. The green bodies were calcined at 300°C to completely remove the porogenic agent. All samples presented porosity higher than 20 % and were characterized by the presence of macropores dispersed in a microstructure formed by β-Si_3N_4, α-Si_3N_4 and wollastonite. The compressive strength and Young's modulus ranged from ~25-358 MPa and ~19-178 GPa, respectively. Both properties had the values reduced with the samples porosity. However, this reduction was most significant for the sample with the highest NH_4HCO_3 content and can be attributed to the formation of a greater number of irregular and interconnected pores. This method is cost-effective for producing porous Si_3N_4 ceramics and is well-suited for industrial-scale production.

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