Sintering of Si₃N₄ nano-powder prepared by plasma synthesis

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Abstract

Nano-sized Si₃N₄ powder coated with Y₂O₃ and Al₂O₃ sintering additives has been sintered by hot pressing and gas pressure sintering at reasonably low temperature. Remarkable influence of used sintering method and heat-treatment regimes on the microstructure was observed. Vickers hardness and fracture toughness was measured by indentation testing method. Correlation between obtained microstructures and mechanical properties was observed.

K e y   w o r d s: ceramics, nitrides, sintering, hardness, toughness

1. Introduction

Polycrystalline silicon nitride and Si₃N₄-based composites are widely studied materials owing to their interesting properties at room and elevated temperatures resulting in good applications potential [1–5]. Generally, dense bulk non-oxide ceramic materials are prepared by liquid phase sintering at relatively high temperatures. Different oxides are usually used as sintering promoters. Most frequently alumina and yttria are used for this purpose [1–3, 6–9].

In the last decade, nano-sized powders were also used for preparation of dense Si₃N₄ ceramics [10–12]. Due to the fine starting powders the final microstructure can be controlled.

Nano-sized grains will be sintered more effectively owing to the high free surfaces, and therefore higher driving force would be realized. Hence the process could be cheaper and more useable for the practical application. Materials with tailored nano-structure can exhibit extraordinary properties. Therefore present research effort is focused on the stabilization of the nano-structure of Si₃N₄ based ceramics.

Two-step sintering method is considered as suitable method for the preparation of Si₃N₄ based ceramics with stabilized nanostructure [10]. Several other ceramic powders have been successfully sintered by two-step sintering method [13–17]. The stabilization of nano-grain size or suppression of grain growth has

been achieved by sintering under high applied stresses [18, 19].

Present paper deals with the densification of Si₃N₄ powder by hot pressing and gas pressure sintering and subsequent characterization of sintered bodies. Fracture toughness and macro-hardness of these materials will be correlated with the observed nano/micro-structure and applied sintering method.

2. Experimental

Nano-sized Si₃N₄ powder was prepared by evaporation of commercially available powders and subsequent condensation of products into nitrogen plasma. Prepared nano-size Si₃N₄ powder was dispersed in liquid medium and mixed with aluminium and yttrium nitrate solution. The deposition of Al(NO₃)₃ and Y(NO₃)₃ on Si₃N₄ grains was controlled by ammonium hydroxide. The dried powder mix was calcinated. The detailed process is described elsewhere [20]. The final powder consists of 91 wt.% Si₃N₄, 6 wt.% Al₂O₃ and 3 wt.% Y₂O₃.

The uniaxially pressed samples (12 mm in diameter and 10 mm high) were embedded in BN and hot pressed at 1750 °C for different time under mechanical load of 30 MPa in N₂ atmosphere. Additionally, cold isostatically pressed sample with the same green body parameters was gas pressure

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Table 1. Sintering conditions

Sample	Sintering	T (℃)	Dwell (hour)	Load (MPa)
S-1	Hot pressing	1750	1	30
S-2	Hot pressing	1750	0	30
S-3	Gas pressure	1750	2	3

Table 2. Characterization of the sintered samples

Sample	Density	Properties	
	$\rho/\rho_{\mathrm{theor}}$ (%)	HV (GPa)	K_{IC} (MPa m$^{1/2}$)
S-1	97.5	15.03 ± 0.64	6.38 ± 0.16
S-2	97.5	16.26 ± 0.32	5.60 ± 0.21
S-3	98.4	16.53 ± 0.13	6.52 ± 0.24

sintered at 1750℃ for 2 h under 3 MPa N_2 atmosphere (Table 1). Densities of sintered samples were measured by Archimedes method in mercury. The theoretical densities were calculated according to the rule of mixtures. The microstructures of polished and plasma etched samples were observed by scanning electron microscopy (EVO-40, Zeiss, Germany). Vickers hardness and fracture toughness were measured using LECO Hardness tester (Model LV-100AT, LECO, USA) by indentation method with loads of 9.8 N and 98 N, respectively. Fracture toughness was calculated using the formula of Shetty [21].

3. Results and discussion

The densities of hot pressed and gas pressure sintered Si_3N_4 nano-powders reach 97 % of theoretical density (Table 2). It can be concluded from the obtained values of densities that the investigated plasmochemically prepared nano-sized Si_3N_4 powder coated with the sintering additives is suitable for liquid phase sintering. On the other hand further optimization is necessary to achieve fully dense Si_3N_4 ceramics body.

Sample S-2 hot pressed without dwell time has an identical density with sample S-1 hot pressed sintered for one hour at 1750℃. It is evident that the powder
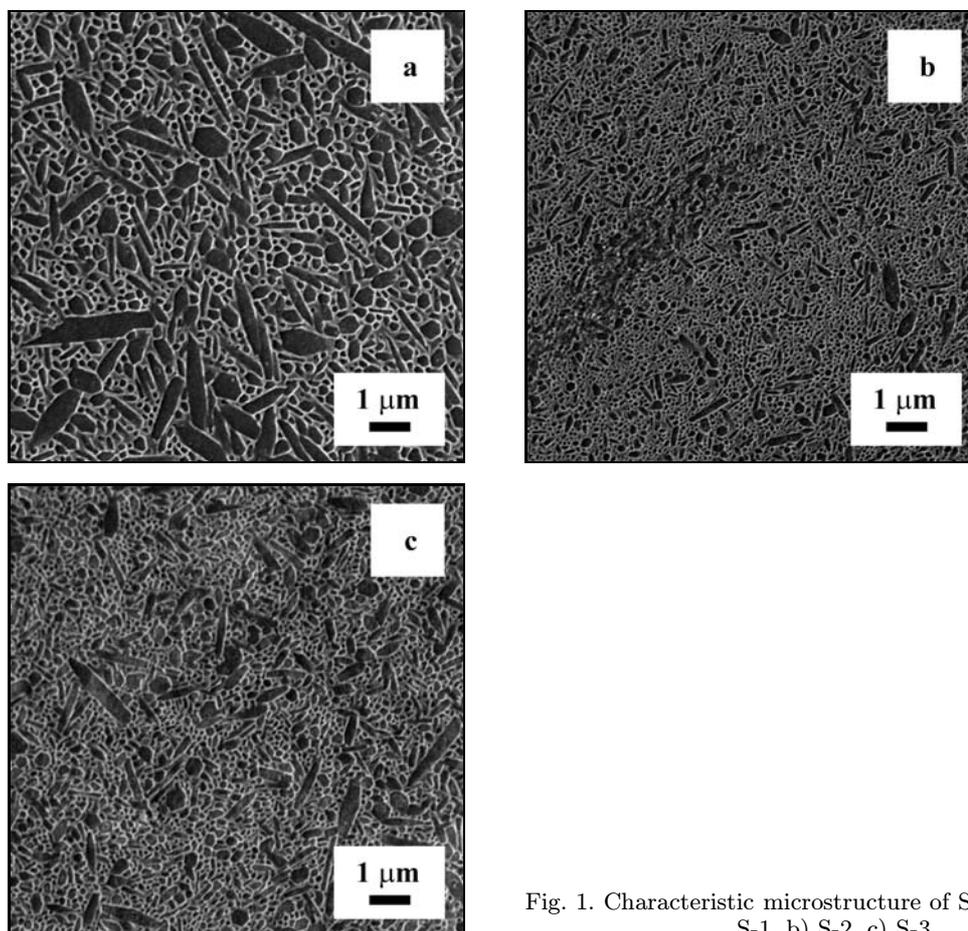
Fig. 1. Characteristic microstructure of Si_3N_4 samples: a) S-1, b) S-2, c) S-3.

was effectively sintered without application of long time sintering, and the plasmochemically prepared nano Si_3N_4 powder is suitable precursor for the short time sintering. The CIP-ed sample S-3 densified by gas pressure sintering for two hours at 1750 °C under 3 MPa N_2 pressure exhibits the highest density from all investigated samples.

The microstructures of sintered Si_3N_4 samples are shown in Fig. 1. All samples exhibit characteristic microstructure containing a large amount of elongated Si_3N_4 grains. Phase analyses confirm that all samples contain β-Si_3N_4 grains only. Strong influence of sintering regimes is evident from the microstructural development. All samples have bimodal microstructure with different amount and aspect ratio of elongated Si_3N_4 grains. The aspect ratio increases in the order: S-2; S-3; S-1. The microstructure of sample S-2 sintered for the shortest time consists of nano-sized Si_3N_4 grains contrary to the other samples, where more intensive grain growth was observed. Although, sample S-2 has also bimodal microstructure, the majority grains have a size close to 100 nm.

All samples were sintered at the same temperature but with different external load during sintering. The sample S-3 sintered by gas pressure sintering for 2 hours with applied 3 MPa external pressure has smaller grains compared with the hot pressed sample S-1 sintered only for one hour. From the observed microstructures it can be concluded that the grain growth of investigated nano-sized Si_3N_4 powder was promoted by the applied external stresses.

The influence of sintering dwell time and applied overpressure were identified as the dominant effects responsible for the formation of the final microstructure of Si_3N_4 ceramics.

Mechanical properties (hardness and fracture toughness) were measured in the middle part of the Si_3N_4 samples with relatively low porosity. The Vickers hardness and fracture toughness of Si_3N_4 ceramics are shown in Table 2. The comparison of hot pressed samples shows expected results. Samples with higher content of elongated grains (S-1) exhibit higher fracture toughness, and *vice versa* samples with finer microstructure (S-2) have higher hardness. It means that the obtained nanostructure of the sample S-2 results in the higher hardness and lower fracture toughness.

Comparison of hot pressed and gas pressure sintered samples shows that the gas pressure sintered sample (S-3) has partially higher hardness than the hot pressed sample (S-2) and negligibly higher fracture toughness compared with the hot pressed sample (S-1). Most probably the residual porosity affected the mechanical properties of investigated samples. The better mechanical properties of the gas pressure sintered sample (S-3) are mainly due to the higher final density.

Comparison of samples shows a general trend that with increasing aspect ratio the fracture toughness increases and the hardness decreases.

It can be concluded that the effective controlling of sintering process is an important technological aspect for tailoring the properties of LPS Si_3N_4 determined practical utilization of advanced ceramics.

4. Conclusion

The density and microstructure of nano-sized Si_3N_4 powder prepared by plasmochemical method coated with the sintering additives (Y_2O_3/Al_2O_3) depends on the sintering conditions. The gas pressure sintered sample has the highest relative density compared with the hot pressed samples. Additionally the hot pressed sample without dwell time achieved the same density as the sample after one hour. It means that the gas pressure sintering and hot pressing without dwell are suitable methods for densification of plasmochemically prepared Si_3N_4 powder.

Final microstructures contain relatively high amount of elongated Si_3N_4 grains. Significant grain growth was observed especially in the case of hot pressed sample sintered for one hour at 1750 °C. Hot pressing without applied dwell time resulted in very fine nano-grain microstructure with small elongated Si_3N_4 grains. Gas pressure sintered sample has finer microstructure than hot pressed sample sintered for one hour, but coarser than hot pressed sample without dwell time.

The observed microstructural differences between samples were formed owing to the different sintering regimes. Especially influence of sintering dwell time and applied overpressure were identified as important effects responsible for formation of final microstructure of Si_3N_4 ceramics.

Generally, the mechanical properties are in correlation with the obtained microstructure. Hot pressed samples with finer microstructure have higher hardness, while samples with elongated grains have higher fracture toughness. The gas pressure sintered sample has partially higher hardness and higher fracture toughness compared with the hot pressed samples with ~ 2 % residual porosity.

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