

Application of Mechanochemical Processing for Preparation of Si₃N₄-based Powder Mixtures

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ABSTRACT

Mechanochemical processing (MCP) involves several high-energy collisions of powder particles with the milling media and results in the increased reactivity/sinterability of powder. The present paper shows results of mechanochemical processing (MCP) of silicon nitride powder mixture with the relevant sintering additives. The effects of MCP were studied by structural changes of powder particles themselves as well as by the resulting sintering/densification ability. It has been found that MCP significantly enhances reactivity and sinterability of the resultant material: silicon nitride ceramics could be pressureless sintered at 1500°C. Nevertheless, a degree of a silicon nitride crystal lattice and powder particle destruction (amorphization) as detected by XRD studies, is limited by the specific threshold. If that value is crossed then particle's surface damage effects are prevailing thus severe evaporation overdominates mass transport at elevated temperature. It is discussed that the cross-solid interaction between particles of various chemical composition, triggered by many different factors during mechanochemical processing, including a short-range diffusion in silicon nitride particles after collisions with other types of particles plays more important role in enhanced reactivity of tested compositions than amorphization of the crystal lattice itself. Controlled deagglomeration of Si₃N₄ particles during the course of high-energy milling was also considered.

Key words : Mechanochemical processing, Silicon nitride, Fine-grained, Low-temperature sintering

1. Introduction

There is a growing demand for ultra-wear resistant and tough structural ceramic materials in applications such as high-speed cutting tools, parts of engine, sealing valves etc. and structural Si-based non-oxides are of special interest because of their exceptional hardness, extraordinary corrosion resistance, low density and high wear resistance. The latter can be significantly improved if fine-grained non-oxide Si-based ceramics could be manufactured.¹⁾ The key factor in acquiring silicon nitride ceramics with grains of a diameter below 1 μm is to suppress the grain growth by application fast densification method (i.e. spark plasma sintering, SPS) or by consolidation conducted at relatively low temperature. The latter is, however, difficult to be accomplished as a consequence of the low self-diffusion coefficient of nitrogen atoms. There are several approaches how to modify the microstructure of the involved structural ceramic components through the nanopowders employment.²⁻⁴⁾ and the careful design of processing,^{5,6)} but the hindrance of the successful and financially acceptable manufacturing routes remain open yet. Nanosized powder is essential in manufacturing the nanostructured ceramic products, moreover, the nanosized particles shorten a diffu-

sion distance during densification of the covalent bonded compound. The major drawbacks of the gas phase derived nanopowders are their high agglomeration, low packing density and enormous problems arising if the homogenous mixing with a minor additive is required. Thus refinement of the silicon nitride ceramic microstructure below one micrometer requires a rapid consolidation such as spark plasma sintering (SPS).^{7,8)} In contrary, pressureless sintering at relatively low temperature could be applied only if the precursor batch shows sufficient densification ability. Therefore, mechanochemical processing (MCP) appears as an attractive and commercially promising method of an effective manufacturing nanocomposites in the form of nanostructured particles.

Mechanochemical processes (MCP) use mechanical energy to activate chemical reactions and structural changes besides particle size reduction. Under the action of cyclic loading, after breaking crystal bonds, MCP engages powder particles into a non-equilibrium state with a relaxation time of 10⁻⁷ – 10⁻³ s and Froes⁹⁾ shows that the departure from equilibrium in MCP is faster than for the rapid solidification. Change of the accumulated energy relaxation from fracture to plastic deformation results in a dramatically increase of the strain followed by the extreme dislocation flow. Accordingly, the elastic strain energy transforms into elastic energy of lattice defects and structural disordering or it can be relaxed by fracturing of brittle material or by the cross-solid interaction if various chemical particles were collided.¹⁰⁾

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Thus the serious damage of the crystalline lattice and reactions at the particle surface apart from the powder particle refinement would be beneficial for lowering densification temperature as diffusion paths are enhanced and shortened respectively.

The results on the mechanochemical treatment of the silicon nitride powder were published by Xin Xu¹¹⁾ and proved higher ability of this compound for densification if SPS technique of densification was applied. As a result of the significant powder particles damage the maximal shrinkage rate values ($-\frac{d(\Delta L/L_0)}{dt}$) increased as much as 20 times from 0.004 s^{-1} (the reference material) to 0.08 s^{-1} for the milled powders. Consequently the fully dense nanoceramic with the grain size around $70 \text{ nm}^{12)}$ was produced after densification. In contrary to the coarse microstructure with elongated $\beta\text{-Si}_3\text{N}_4$ grains the isometric but nanostructured silicon nitride ceramics show higher hardness (18.3 GPa) and better ductility than that reported elsewhere.¹²⁾

Our research showed that planetary milling of the precursor mixture ($\text{Si}_3\text{N}_4+\text{AlN}+\text{Y}_2\text{O}_3$) results in the significant increase of the specific surface area and strongly depends on the milling time apart from the applied energy (rotational speed of the vial, ball-to-powder ratio, acceleration in the chambers etc.).¹³⁾ Reduction of yttria and aluminium nitride crystallites is observed after the short milling time while α or $\beta\text{-Si}_3\text{N}_4$ crystal lattice remains more resistant to the applied mechanochemical treatment¹¹⁻¹³⁾. Several types of the defective crystal lattice were evidenced by examinations in a transmission microscope: dislocations, damaged surface of individual particles, amorphization.¹⁴⁾ The increasing amorphization of the β or $\alpha\text{-Si}_3\text{N}_4$ crystal lattice was evidenced by swelling the unit cell volume. Our latest results¹⁵⁾ showed miscellaneous effect of MCP on particles agglomeration if a range of milling energy was applied. This paper aims at the research how those results are related to the course of the complex reactions of solution/precipitation accompanied by densification process.

2. Experimental Procedure

A mixture of commercial powders of $\alpha\text{-Si}_3\text{N}_4$ (M11 grade by H. S Starck) and additives as: 5.7 wt% of high purity AlN (fine C grade by H. S Starck) and 5 wt% of Y_2O_3 (fine C grade by H. S Starck) powders were chosen. Aluminium nitride has been chosen as an additive since some oxidation of nitride particles during MCP could have occurred and oxygen content should be kept low. The mixture of methyl-ethyleneketone (MEK) (butanone-Sigma Aldrich) and ethanol (ET, 99.8vol% by POCH) in 66/34vol% ratio was used as a solvent for preparation of a suspension. Hypermer KD1 (3 wt%) was added to MEK/ET suspension as a surfactant. Homogenization process was a multi stage one and it consisted of the following steps : mechanical mixing of the suspension on a roller bench for 24 h, followed by ultrasonical treatment for 2 h (Branson Sonifier W-450D) and finally evaporation in a laboratory dryer at 110°C . Dried powder was then milled in

a high energy micro-planetary mill (Pulverisette Premium Line 7 by Fritsch). The vial with Si_3N_4 lining and silicon nitride grinding balls of 5 mm diameter were used in a high purity argon atmosphere. MCP was performed at a rotation speed of 1000 rpm for 30-360 min. Ball-to-powder ratio (B/P) was 4:1 or 8:1. The resultant powder was then compacted into pellets of 3-5 mm height and 10 mm diameter by preliminary uniaxial pressing at 50MPa followed by cold isostatic pressing (CIP) at 300MPa. The resultant pellets were thermally treated in air at 500°C in order to decompose and to remove organic additives. Subsequently, samples were pressurelessly sintered in the graphite chamber furnace (Thermal Technology) in a powder-bed ($\text{BN/Si}_3\text{N}_4$) at temperature of 1500°C in high purity (99.999%) nitrogen flow for 60 to 240 min. Choice of that rather simple technique of densification was supported by its high potential for practical application.

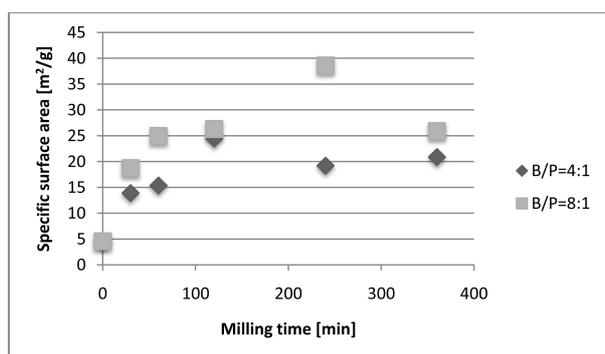
The specific surface area of the milled powders was examined by BET method (ASAP 2000, Micromeritics). Morphology of the powder particles was observed in the scanning (SEM, Hitachi S-4200) and transmission (HR-TEM, Joel JEM 3010) microscopes. Specimens for TEM were carbon coated and observed in a JEOL model 100B transmission electron microscope at an accelerating voltage of 100 kV. Electron diffraction was measured by the means of selected area diffraction (SAD) and the patterns were resolved with the use of the ELDYF program. The phase composition was determined from Rietveld refinement of XRD data obtained using an Philip-Panalytical X-pert-PRO system with a continuous step scan. The accuracy of the calculated phase content was $\pm 0.1 \text{ wt}\%$. The apparent density of the sintered specimens was measured using the Archimedes method in water. Relative density was calculated from the mixture rules and was close to 3.29 g/cm^3 . X-ray diffraction (XRD) ($\text{Cu K}\alpha$ radiation) was performed on a polished cross-section of the specimens. Hardness was measured by Vickers indentation method in a HV10 test (load of 98N) in Struers Duramin A 300 equipment. Elastic modulus was obtained from the ultrasonic wave velocity measurement. Fracture toughness K_{IC} was estimated from the cracks length measurement based on Anstis's formula after indenting at the same load as for hardness test for 15 s.¹⁶⁾

3. Results and Discussion

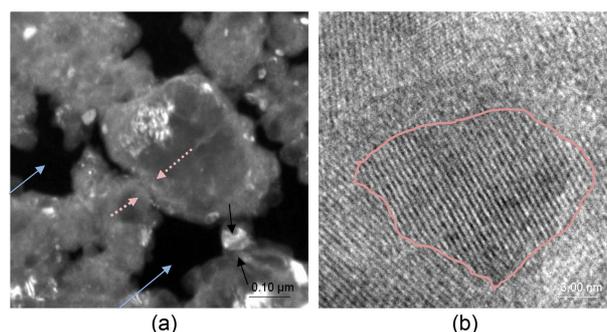
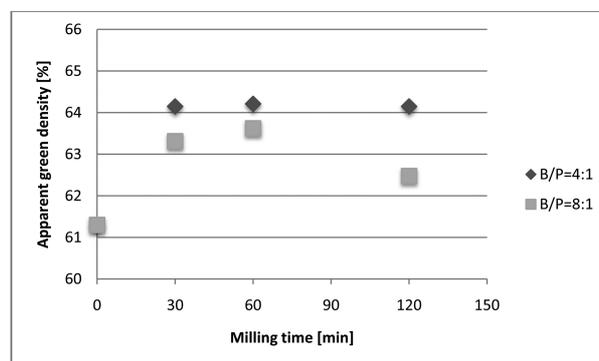
Outcome of the mechanochemical processing with various B/P ratio was examined by measurement of the specific surface area (SSA) and XRD studies. Elongation of the milling time leads to the substantial changes of the crystal lattice of the involved powders: decrease of the crystallite size or the large-scale amorphization as yttria or AlN phases were undistinguishable in the XRD pattern (Table 1). Alteration of the phase composition due to the course of milling is obviously related to the growing amorphization of the least resistant powders of the milled batch. Fig. 1 shows the effect of the milling time on development of SSA if two various B/

Table 1. Phase Composition and Crystallite Size of the Powders Mixture after Milling for 0.5 and 6 h with 4:1 or 8:1 Ball-to-powder Ratio

Milling time [min]	B/P ratio	Phase composition [wt %]				Crystallite size [nm]	
		α -Si ₃ N ₄	β -Si ₃ N ₄	Y ₂ O ₃	AlN	α -Si ₃ N ₄	β -Si ₃ N ₄
0	0	78	10.2	7.4	4.4	150	100
30	4:1	80.4	11.1	5.8	2.7	130	64
360	4:1	87.2	12.8	-	-	77	30
	8:1	92.4	7.6	-	-	49	-

**Fig. 1.** Specific surface area of the precursor powder after milling with various B/P ratio (4:1 and 8:1) versus the milling time.

P ratios were applied. As expected, higher energy milling (B/P=8:1) resulted in more significant growth of SSA in comparison to lower energy milling results. However, development of SSA becomes ineffective after the given milling time. Two explanations of such behavior are possible: formation of the new, no-gas accessible clusters due to shear stresses during high energy milling or secondary welding of nanoparticles as a result of high-energy collisions. TEM studies (Fig. 2(a)) show formation of the closed clusters with the limited access for a gas permeability during the specific surface measurement by the BET method. The type of bonding between the particles as shown in Fig. 2(a) could be of the second order (adhesive bonding – dotted line) or the chemical bond could form if two different chemical species have been in contact during high-energy collision. Fig. 2(b) shows HR-TEM image of the two diverse particles. The smaller particle with diameter of 10-15 nm is embedded in the larger amorphous particle. However, as a consequence of their serious damage of the crystal lattice, recognition of those species was unattainable via the applied method. In summary of the characterization of the mechanochemically processed powders we could assume that several consequences to powder particles occurred: reduction of powder particles, formation of agglomerates, amorphization of the crystal lattice and welding of particles. The latter could result in a short-range transfer of atoms and formation of new chemical bonds. Previously we reported formation of the new chemical bonds in the similar system as it was evidenced by the FT-IR results.¹³ It must be, however, stressed

**Fig. 2.** Morphology of powder particles after milling for 360 min with B/P= 8:1, (a) dark-field TEM image, (b)HR-TEM image.**Fig. 3.** Apparent green density of the samples compacted from the powders after various milling time and ball-to-powder ratio.

that those effects are related to the applied milling parameters (ball-to-powder ratio, the time of milling) and one of them could overcome the others during the course of milling.

Compaction of the ensuing powder resulted in the high green density (Fig. 3), more than 60%. Those values are significantly higher in comparison to the reported values of compacted nanopowders: 41%²⁾ or conventionally mixed submicro-sized powders: 47.7%.¹⁷⁾ The course of green density versus the powder milling time resembles curves of powders SSA after milling. Nevertheless, higher packing density was attained as a result of lower SSA thus we could assume that breaking of agglomerates was more important for better packing of powder particles than other effects of MCP.

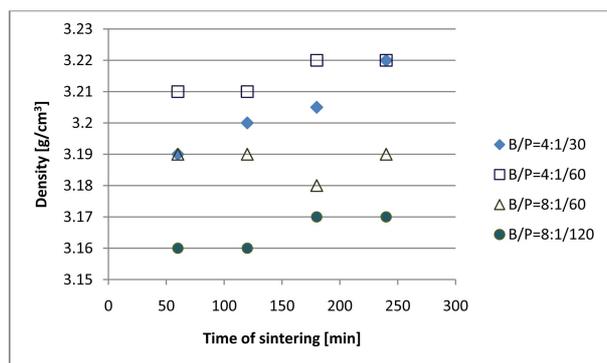
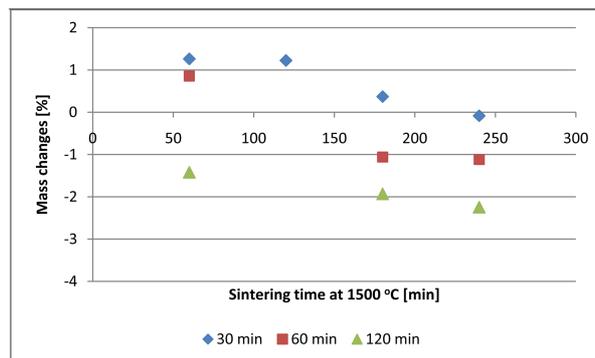


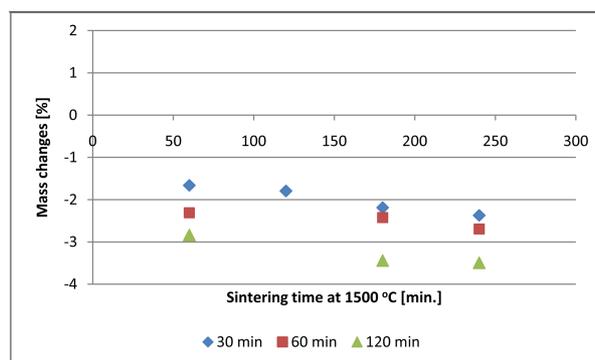
Fig. 4. Density of specimens prepared from precursor after various milling time and different ball-to-powder ratio sintered at 1500°C.

All specimens sintered for 360 min at 1500°C showed mono-phase composition of β -sialon with a low z -value of 0.2. Formation of β -sialon instead of β - Si_3N_4 could stem from both: higher nitrogen content in the liquid because of AlN presence as well as it could result from more enhanced dissolution of additives due to their amorphization.

Densification of the resultant compacts was studied by examination of their linear dimension & density changes, accompanied mass losses as well as mechanical properties of the resultant ceramics. Densification outcome demonstrates expected results if powders were milled with moderate energy, i.e. B/P ratio = 4:1 (Fig. 4) and reasonable properties of the resultant ceramics (Table 2). Elongation of the sintering time leads to higher densification thus sintering ability is controlled by the previously applied milling time: the longer milling time, the higher density at each stage of sintering. Those results are in contrary to the compaction ability (Fig. 3) and to the surface area of the processed powders (Fig. 1): the higher SSA, the slightly lower green density was experienced but the higher density after sintering was attained. Thus we could conclude that the primary inhomogeneities in the compacted specimens, as evidenced by lower green density, were of less importance in comparison to the high densification ability of the powders with high SSA. Those observations are supported by the mass changes during pressureless densification (Fig. 5(a)): the low milling time and the low SSA produced mass increase during sintering for 60-180 min. It was not the case if the precursor mixture was milled for 120 min or if longer sintering time was applied. Mass increase during sintering of silicon nitride in the powder bed indicates evaporation/condensation processes and that type of mass transport is closely related to the surface state of silicon nitride parti-



(a)



(b)

Fig. 5. Mass changes of compacted powders derived from B/P = 4:1 (a) and B/P= 8:1 (b) milling regime for 30; 60 and 120 min after thermal treatment at 1500°C for various time.

cles. What is more, mass increase was noted for specimens with relative density close to 97% i.e. in the final stage of densification, but we must conclude that those values resemble, nevertheless, the initial stage of sintering. According to the classical theory of silicon nitride reaction sintering the first stage is related to the particle rearrangement within the initial liquid and the extent of shrinkage depend on the volume of liquid.¹⁸⁾ Consequently, evaporation/condensation process could dominate over dissolution if the silicon nitride particle surface was damaged and it was not accompanied by the sufficient cross-surface interaction between the involved particles during MCP. Continuation of sintering over 60 min led to a slight but steady Si/SiO evaporation related to the significantly reduced surface area of specimens with relative density of 97%. If the longer milling time (120 min) with B/P ratio = 4:1 was applied during MCP then the mass transfer via evaporation/consolidation during the initial densification stage was successfully suppressed and relative density of 98% was attained after sintering for

Table 2. Properties of Silicon Nitride Ceramics Prepared from Medium-energy Milled Powders (B/P=4:1, milling time: 30 min)

Temperature of sintering [°C]	Sintering time [min]	Apparent density [g/cm ³]	Hardness [GPa]	K_{1C} [MPa*m ^{1/2}]	Elastic modulus [GPa]
1500	240	3.21	17.6±0.6	6.38±1.04	314
1500	360	3.22	17.7±0.5	6.05±0.66	309

60 min.

On the contrary, sintering of the precursor after the high-energy milling with B/P ratio = 8:1 led to lower densities in comparison to the powders milled with B/P ratio = 4:1 (Fig. 4). The higher SSA of the milled precursor, the lower density was produced after sintering and higher mass losses were measured (Fig. 5(b)). It is clear that surface and crystal defects played more significant role during the first step of pressureless sintering than the cross-surface interaction effects. Accordingly, there is an upper limit of the mechanochemical processing effects in Si-based powders as increased volatility of those compounds at higher temperature must be considered.

4. Summary

Powder mixture of α -Si₃N₄, 6 wt% Y₂O₃, 5.7 wt% AlN was subjected to mechanochemical processing under 1000 rpm, ball-to-powder ratio 4:1 and 8:1 for 60-360 min, followed by sintering in powder bed in flowing nitrogen at 1500 °C for 60-360 min. It was found that increasing energy input (ball-to-powder ratio, milling time) creates several effects: diminution of the particles size and increase of the surface area, lattice crystal defects and cross-solid interaction effects, though prolongation of the milling time results in secondary welding of particles and re-agglomeration. The milled powders can be easily compacted to high green density over 60% and consolidated to 98 % apparent density by pressureless sintering at 1500°C. Pressureless sintering of the mechanochemically processed precursor is sensitive to the parameters of powder milling since two processes are competitive during the initial stage of sintering: liquid formation by dissolution of sintering additives and silicon nitride volatilization. If the high specific surface area of the precursor powder over 40 m²/g was attained than silicon volatilization prevailed and relative density below 96% was noted.

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