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## CHARACTERIZATION OF THE MECHANOCHEMICALLY PROCESSED SILICON NITRIDE-BASED POWDERS

### WŁAŚCIWOŚCI PROSZKÓW AZOTKU KRZEMU AKTYWOWANYCH MECHANOCHEMICZNIE

Nanostructured silicon nitride and aluminium nitride powder mixtures have been successfully produced by high-energy mechanical activation in the planetary mill. The effect of planetary milling parameters (time, ball-to-powder ratio, surfactants addition) and means of deagglomeration by the ultrasound disintegration (type of dispersant, the ultrasonic action) were studied. The resultant powders were examined by XRD, SEM and TEM as well as the specific surface area (BET) was measured and grain size distribution was analyzed. It has been found that significant agglomeration occurred in the samples milled with the highest energy accompanied by the severe destruction of the crystal lattice. The results show the crucial effect of dispersant action for a one-modal distribution of the milled powders.

*Keywords:* agglomeration, mechanochemical processing, silicon nitride

Proces mechanochemiczny w młynku planetarnym został z powodzeniem zastosowany do otrzymywania nanostrukturalnych proszków w mieszaninie azotku krzemu i glinu. Badano wpływ parametrów procesu mielenia i deaglomeracji takich jak: czas mielenia, prędkość obrotowa młyna, średnica mielników, stosunek mielników do proszku, rodzaj i ilość dodatków powierzchniowo czynnych, czas i energia dezintegracji ultradźwiękowej na właściwości proszku po procesie. Przeprowadzono badania XRD, SEM, oraz TEM, badania powierzchni właściwej metodą BET oraz rozkład dystrybucji ziarn metodą laserową po procesie mechanochemicznym prowadzonym z różną energią. Stwierdzono, że w wyniku zastosowania najwyższej energii mielenia następowało znaczące zniszczenie sieci krystalicznej w ziarnach proszku, ale towarzyszyło im zjawisko znacznej aglomeracji. W uzyskaniu jednomodalnego rozkładu ziarnowego mieszaniny proszków kluczową rolę odgrywa działanie zastosowanego środka dyspergującego.

### 1. Introduction

Silicon nitride and related sialon ceramics are well known and excellent engineering materials successfully manufactured by a variety of methods [1]. However, their production methods suffer from low efficiency thus the high-pressure assisted techniques are necessary to overcome low sinterability and silicon nitride high partial pressure at elevated temperature. Therefore any new means of a densification increase would be interesting in that area. One of an attractive and a suitable method for increasing sinterability of silicon nitride-based powders is mechanochemical processing (MCP) of the mixture of the starting powders [2-3]. Application of the MCP method is useful in preparation of powder mixtures for synthesis [4], alloying [5] and other diverse processes [6].

Despite the very promising results on the effects of MCP on densification of silicon nitride ceramics, the latest studies showed the crucial behaviour of particles agglomeration during mechanochemical action on the properties of the resultant powder [7]. It has been found that milling with moderate energy is successful in breaking agglomerates and formation of the mono-modal dispersion of particles in contrary to the high-energy milling. The latter produces an increasing number of agglomerates, a decrease of the specific surface area and worse homogeneity of the shaped items. Thus further research on the effects of high-energy mechanochemical processing are necessary for the multicomponent mixtures as it occurs in the case of silicon nitride-based mixtures. The present studies concentrate on the effects of dispersant addition, time of milling and ball-to-powder ratio on the effects of MCP application to  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>-based mixture.

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## 2. Experimental

The initial commercial powders of  $\alpha$ - $\text{Si}_3\text{N}_4$  high purity (M11 with median size  $D_{50}=0,5-0,7 \mu\text{m}$  by H. S Starck), AlN high purity (fine C grade with median size  $D_{50}=9.5 \mu\text{m}$  by H. S Starck),  $\text{Y}_2\text{O}_3$  (fine C grade with median  $D_{50}$  size below  $0.9 \mu\text{m}$  by H. S Starck) were used for blending and MCP.  $\alpha$ - $\text{Si}_3\text{N}_4$  powder was contaminated by about 10 wt% of  $\beta$ - $\text{Si}_3\text{N}_4$ . Weighted batches of 89.3 wt%  $\alpha$ - $\text{Si}_3\text{N}_4$  + 5.7 wt% AlN + 5.0 wt%  $\text{Y}_2\text{O}_3$  were prepared. An azeotropic mixture of methylethyleneketone (MEK) (butanone-Sigma Aldrich) and ethanol (ET, 99.8vol.% by POCH) in 66/34%vol ratio was used as a solvent for preparation of a suspension. KD1 hypermer (Imperial Chemical Industries PLC, UK) and (triethyl phosphate 99,8% by Sigma-Aldrich) were used as dispersants. The powders were batched, dispersed in MEK/ET liquid with addition of a KD1 surfactant (3 wt% of powders weight) or without any dispersant, mixed on a roller bench for 48 hours, ultrasonicated (Branson Sonifier W-450D) for 2 hours and finally evaporated in a laboratory dryer at  $110^\circ\text{C}$ . Dried powder mixture was then milled in a high energy planetary mill (Pulverisette Premium Line 7 by Fritsch) in a 80 ml silicon nitride vial with  $\text{Si}_3\text{N}_4$  grinding balls of 5 mm diameter and vial filling of 20 vol.%. MCP was performed at a rotation speed of 1000 rpm for 0.5-6 hours. The milling was performed in 15 min intervals followed by approximately 30 min breaks for free cooling down. Ball-to-powder (B/P) ratio was limited to the medium-energy range of 4:1 and the high energy range of 8:1. The powders with the longest milling time (6 hours) were then annealed at  $500^\circ\text{C}$  for 2 hours in or-

der to remove any organic constituent. After dispersion in water they were analysed for the particle size distribution. Then they were dispersed again in MEK/ET solvent with KD1 or with triethyl phosphate (TP), they were ultrasonically treated and finally the particle size distribution was measured.

Grain size distribution of dried powders was performed in water suspension (Mastersizer 2000, Hydro S, Malvern Instruments Ltd), after the 2 hours ultrasonification. 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, JEOL JEM 3010) microscopes. 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  $\pm 0.1 \text{ wt}\%$ .

## 3. Results and discussion

Particle size distribution of the initial powders shows tri-modal distribution independently on KD1 dispersant addition. The main population of particles is close to a diameter of  $8 \mu\text{m}$  and must be related to agglomeration of the main  $\alpha$ - $\text{Si}_3\text{N}_4$  component with some input from rather coarse AlN particles (Fig. 1). The coarser population is centred at  $100 \mu\text{m}$  and obviously must be ascribed to large agglomerates of various particles after dispersion in water for particle size distribution measurement. The population of the finest particles is centred at  $0.25 \mu\text{m}$ .

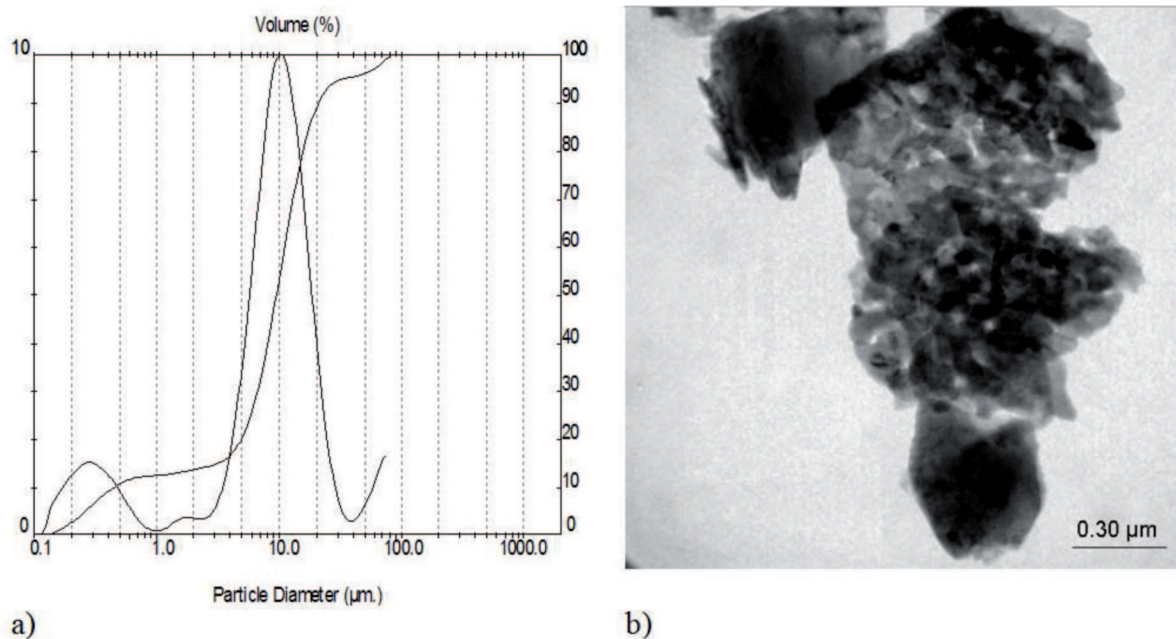


Fig. 1.  $\alpha$ - $\text{Si}_3\text{N}_4$ - $\text{AlN}$ - $\text{Y}_2\text{O}_3$  mixture before milling: a) particle size distribution; b) morphology of agglomerate, TEM

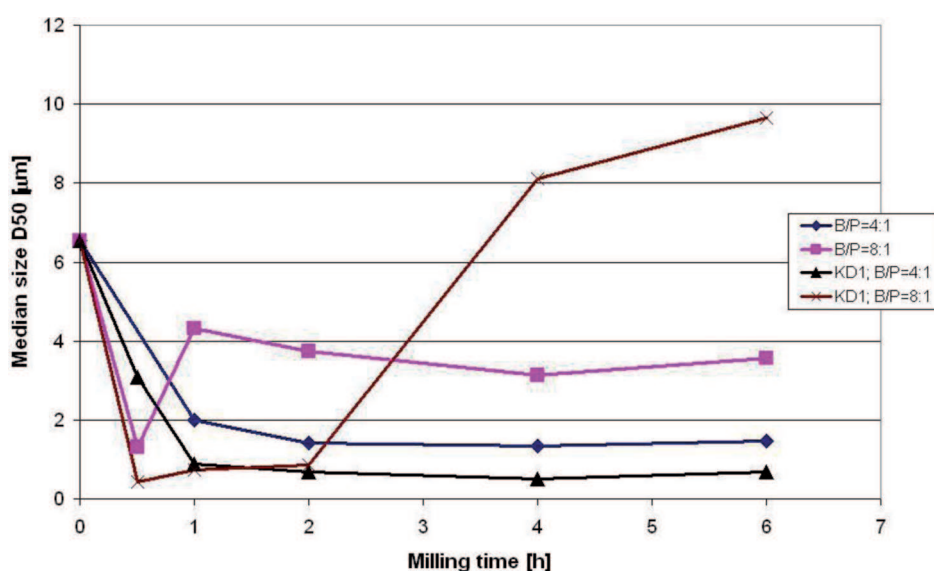


Fig. 2. Median size ( $D_{50}$ ) of the powder particles after milling with moderate (B/P=4:1) and high (B/P=8:1) milling energy with or without KD1 dispersant addition

Mechanochemical processing involves substantial changes in particles behaviour. Median size ( $D_{50}$ ) after the given milling parameters was chosen for presentation of particle diameter changes. They are presented in Fig.2. The medium milling energy (B/P=4:1) is effective in breaking agglomerates and addition of surfactant is helpful in that reaction. However, high milling energy as expressed by B/P=8:1 is operative only during the very short time interval and afterwards the intensive agglomeration occurs. It was deduced previously that agglomeration was related to the decomposition of the

lyophilic part of KD1 hypermer [7] but the present studies show similar behaviour for the mixtures without any dispersant. Thus prolonged milling with high energy results in an increasing number of agglomerates since  $d_{50}$  value grows. It is interesting to note that agglomeration is more intensive in the mixtures with KD1 dispersant after its decomposition in comparison to the mixtures without any dispersant.

The following changes of the particle size distribution after heat treatment and repeated dispersion in MEK/ET with KD1 or triethyl phosphate are shown in

Table 1. They obviously show that removal of the organic dispersant residuals makes dispersion of particles worse in comparison to the non-heat-treated mixtures. On the other hand, if none dispersant was used before MCP, heat treatment did not lead to agglomeration.

Application of dispersant after heat treatment is reasonable only if TP was used. The relevant  $D_{10}$  and  $D_{50}$

values are of the same order independently on the B/P ratio applied in MCP or usage of KD1 dispersant and a nice mono-modal particle size distribution could be observed. Thus application of dispersant before MCP is questionable but it is reasonable for dispersion of powder particles after MCP.

TABLE 1

Changes of particle size distribution after heat treatment at 500°C and subsequent dispersion in MEK/ET with KD1 or TP addition; particle size distribution is expressed in particle size of  $D_{10}$  and  $D_{50}$  measures

Milling parameters	Particle size diameter [ $\mu\text{m}$ ]					
			After milling for 6 hrs	After heat treatment at 500°C	KD1	Phosphate ester
Without initial dispersant	4:1	$D_{10}$	0.44	0.36		
		$D_{50}$	1.47	1.27		
	8:1	$D_{10}$	0.57	0.56		0.37
		$D_{50}$	3.55	2.67		0.93
With KD1 as an initial dispersant	4:1	$D_{10}$	0.22	0.39	2.36	0.39
		$D_{50}$	0.67	1.18	5.59	0.90
	8:1	$D_{10}$	0.39	0.62	3.07	0.40
		$D_{50}$	9.65	5.33	9.42	0.90

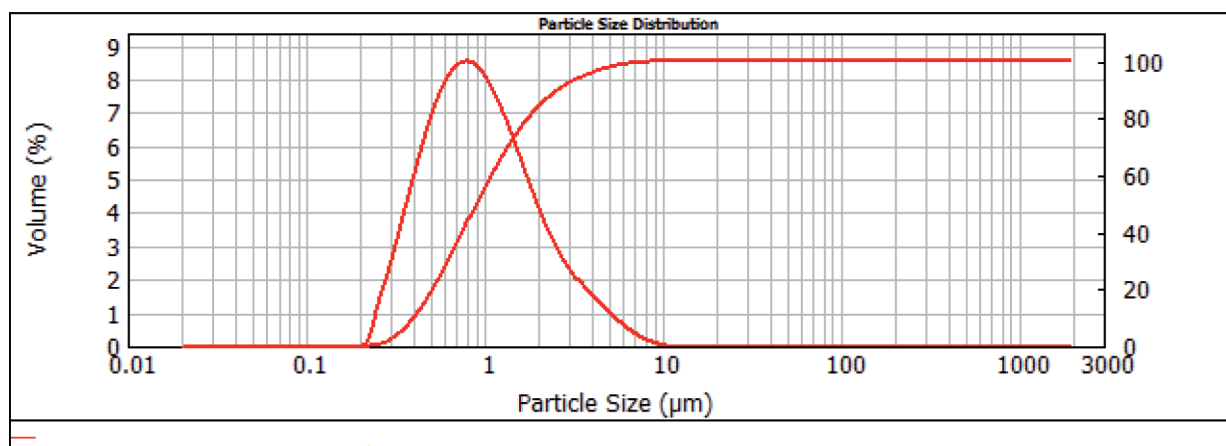


Fig. 3. Mono-modal particle size distribution after 6 hours milling with B/P ratio 4:1 after heat treatment and addition of triethyl phosphate as dispersant

TABLE 2

Phase composition, crystallite size and lattice parameters of the powders mixture after milling for 0.5 and 6 hrs with 4:1 or 8:1 ball-to-powder ratio

Powder		Phase composition [wt %]				$\alpha$ -Si <sub>3</sub> N <sub>4</sub>			$\beta$ -Si <sub>3</sub> N <sub>4</sub>		
		$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	$\beta$ -Si <sub>3</sub> N <sub>4</sub>	Y <sub>2</sub> O <sub>3</sub>	AlN	Crystallite size [nm]	Unit cell: a [Å]	Unit cell: c [Å]	Crystallite size [nm]	Unit cell: a [Å]	Unit cell: c [Å]
Initial	–	78.0	10.2	7.4	4.4	150	7.7523	5.6193	100	7.6044	2.9032
30 min	4:1	80.4	11.1	5.8	2.7	130	7.7521	5.6190	64	7.5067	2.9062
360 min	4:1	87.2	12.8			77	7.7534	5.6203	30	7.6105	2.9086
	8:1	92.4	7.6	–	–	49	7.7552	5.6206	*	7.6220	2.9034

\*) – impossible to calculate with the applied method

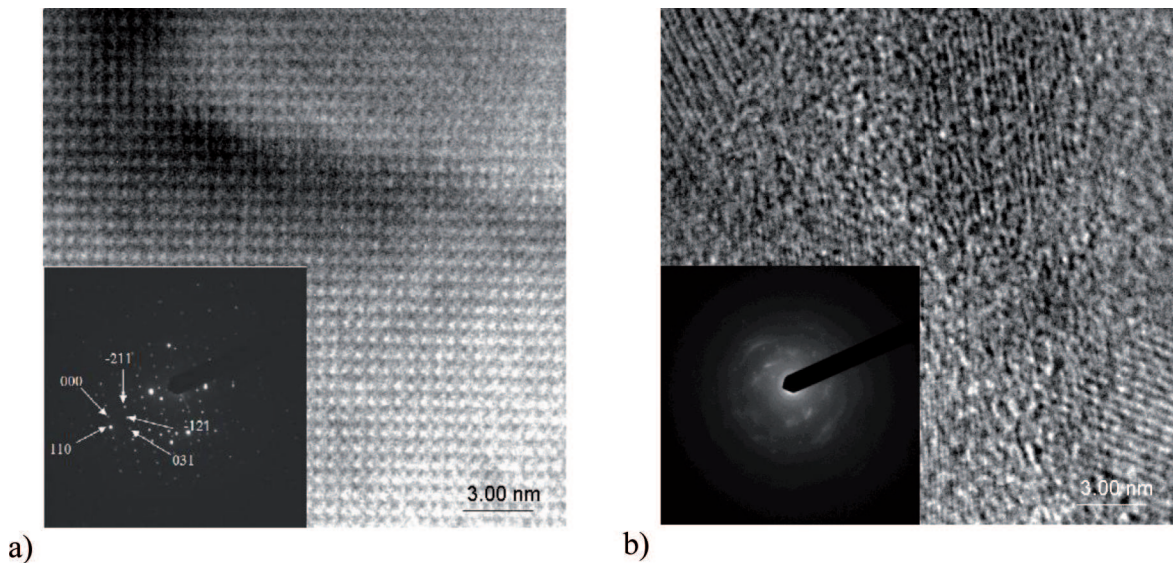


Fig. 4. HR-TEM images of the crystal structure of the Y<sub>2</sub>O<sub>3</sub> particle before (a) and after (b) milling with high energy

Differentiation between the applied energy on the effects of MCP could be studied by comparison of the resultant phase composition and changes of crystallite size of the main components (Table 2). First, variation of the phase composition must be clear out: slight deviation from the initial phase composition in the blended mixture can be related to nonhomogeneous distribution of the low-fraction components. However, further changes of the phase composition after milling must be related to the effects of MCP. Yttria and aluminium nitride were not distinguishable after the longer milling time thus the increase of the silicon nitride content was apparent. It is assumed that distortion of the crystal lattice of both components was significant and resulted in amorphization.

The crystallite size was calculated only for the both silicon nitride polymorphs. The results in Table 2 show that amorphization, as measured by the crystallite size diminution, was more pronounced in  $\beta$ -Si<sub>3</sub>N<sub>4</sub> than in

the alpha polymorph. This behaviour can be related to the higher hardness of the alpha form. Other symptoms of amorphization due to the milling with high energy are noticed for changes of the crystal lattice parameters. Increase of both parameters of the  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> unit cell is ascribed to a growing number of crystal lattice defects, as it is demonstrated in Fig. 4 for yttria particle.

Slightly different behaviour was observed for deformation of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> as changes of both parameters were not consistent and rather some deformation by texturing is expected which is coherent with its crystal structure. In addition, the internal stresses must have been induced in the crystal structure since calculation of the crystallite size from the diffraction lines broadening was not possible for the specimens milled for 6 hrs with the high B/P ratio.

#### 4. Summary

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- In summary, the following conclusions can be given:
- Mechanochemical processing of the silicon nitride-based powders leads to the significant destruction of the crystal lattice and reduction of the crystallite size. The extent of that destruction depends on the applied milling energy and time of milling as well as it is related to the mechanical properties of the given compound. Amorphisation of yttria and AlN occurred to a large extent.
  - Application of a dispersant and deagglomeration of the blended powders before mechanochemical treatment is questionable as decomposition of that dispersant due to the extensive milling does not prevent formation of agglomerates during MCP
  - Dispersion of the mechanochemically processed powders is possible after application of the relevant dispersant and ultrasonical treatment

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