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Preparation and processing of doped AlN nanopowders

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Abstract. The aim of this work is improvement of sinterability of aluminium nitride by combining spark plasma sintering with using nanosized particulate composites prepared by simultaneous evaporation of Al and Y_2O_3, Gd_2O_3 and YF_3 additives in radio-frequency nitrogen plasma. This approach allows to fabricate fully dense AlN materials at 1400 °C with holding time of 2 min despite the reduction of rare-earth compounds and formation of YN and GdN phases in the plasma flow. Besides AlN phase, the prepared materials contain secondary phases aluminium oxynitride, $Y_3Al_5O_{12}$, $GdAlO_3$ or α-Al_2O_3, depending on the used additive.

Key words: plasma synthesis, nanosized AlN, sintering additives, SPS sintering, phase composition.

1. INTRODUCTION

Aluminium nitride ceramics is an attractive material for electronics industry due to high thermal and very low electrical conductivity and the thermal expansion coefficient similar to silicon [1]. High melting point, good thermal stability and corrosion resistance of molten aluminium and cryolyte ensure a growing application of AlN in other fields. AlN finds applications in producing composite materials with TiN and SiC [2] or as binder for cubic boron nitride [3]. Besides that, AlN as a wide gap material has promising optical characteristics [4].

The physical and mechanical parameters of AlN are strongly influenced by chemical purity, density and microstructure. Manufacturing of dense AlN ceramics without additives by using pressureless sintering methods is a difficult task due to the low diffusivity in the solid state and partial decomposition of the

nitride at temperatures above 1800 °C. In order to improve density and to reduce sintering temperature, various sintering aids such as Y_2O_3, YF_3, CaO and CaF_2 have been used [5–7]. The sintering additives reduce the sintering temperature to 1600 °C and improve the microstructure of ceramics.

Further reduction of the sintering temperature and formation of nano-structured ceramics can be achieved by using nanosized powders and the spark plasma sintering (SPS) method [8].

Combined use of nanosized raw powders, sintering additives and spark plasma sintering could be a promising approach for manufacturing nanostructural AlN ceramics.

However, uniform mixing of AlN with a small amount of additives, especially in the case of the nanosized powders, is problematic.

The aim of the present work was to investigate characteristics and SPS sintering behaviour of nanosized AlN and its particulate composites prepared by combining plasma chemical synthesis of AlN by mixing with additives in the vapour phase.

2. EXPERIMENTAL

The gas phase synthesis of AlN-based particulate nanocomposites was performed in inductively coupled nitrogen plasma (99.99) using a custom-built technological apparatus described in [9]. The aluminium powder (99.6%) with particle size in the range of 40–63 μm and Y_2O_3, YF_3 or Gd_2O_3 additives (Treibacher GmbH) with particle size in the range of 10–40 μm was mixed by using a planetary laboratory mill (Retsch PM 400) and injected into the plasma flame (nitrogen 99.99) by carrier gas. The formation of AlN and additive particles from vapours and their growth was controlled by introducing ammonia into the vapours region.

The nanoparticles were sintered by using the SPS (Sojitz Corp.) technique at 1200–1700 °C. The powder was filled up into cylindrical graphite die (inner diameter of 40 mm, outer diameter of 80 mm). The applied pressure was 30 MPa and maintained constant during the whole densification process in the SPS apparatus.

Chemical and phase composition of the samples were determined by chemical, microXRF analysis (EDAX) and X-ray diffraction analysis (Bruker AXS). The content of oxygen was determined by using Eltra ON900 oxygen/ nitrogen determinator. The particle size and grain size of the sintered ceramics were studied by TEM and SEM. The specific surface area was determined by the argon adsorption-desorption method. The average particle size was calculated from these data. The density of the sintered ceramics was found by the Archimedes method.

3. RESULTS AND DISCUSSION

According to the chemical and XRD analysis, the formation of particles from the vapours phase results in obtaining nanosized AlN-based powders, which characteristics depend on introduced additives. The chemical composition of the powders is close to theoretical and content of components is practically indentical for ten samples taken from the definite powder. This indicates that distribution of components in the samples is uniform. The AlN and AlN-YF_3 system samples contain 0.9–1.2 wt% of oxygen as admixture. The source of the oxygen admixture is aluminium raw powder containing 0.6 wt% of oxygen and oxygen that was adsorbed from air.

The XRD analysis shows that simultaneous evaporation of the mixture of aluminium and additives influences XRD patterns of the powders. The XRD patterns of all samples besides AlN diffraction maxima show YN or GdN maxima (Fig. 1) independently of the content of the additives in the raw mixture (Table 1).

That means that reduction of Y_2O_3, Gd_2O_3 or YF_3 occurs by aluminium at high temperature and presence of nitrogen and ammonia promotes formation of yttrium and gadolinium nitrides. Additionally the prepared products should contain aluminium oxide or oxynitride and fluorine compounds, which are X-ray amorphous.

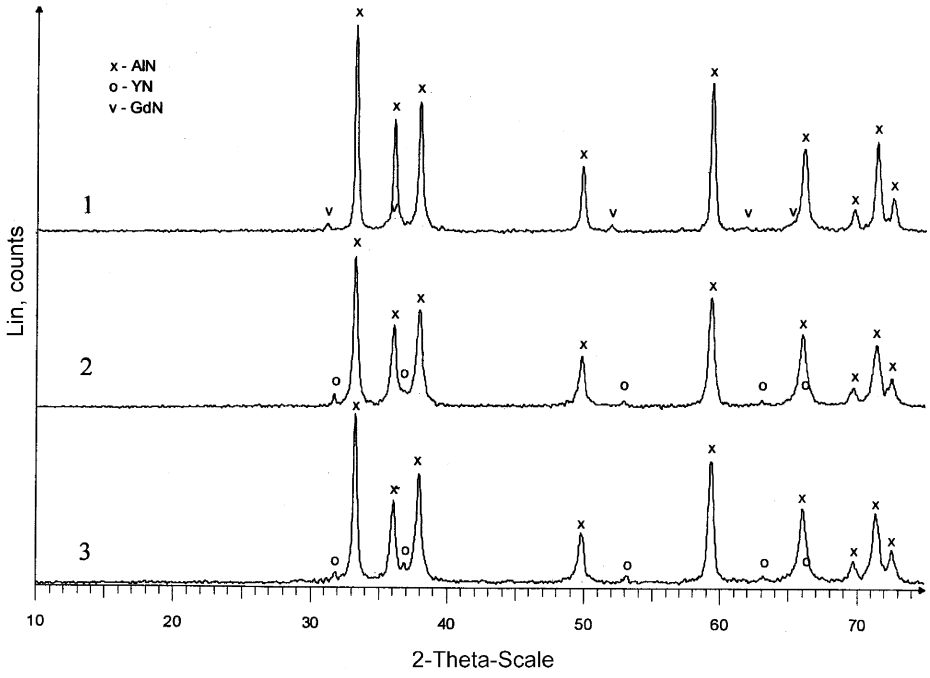

Fig. 1. XRD patterns of particulate nanocomposites prepared from Al/Gd_2O_3 (1), Al/YF_3 (2) and Al/Y_2O_3 (3) mixtures.

Table 1. Specific surface area (SSA), average particle size (*d*) and phase composition (XRD) of AlN particulate nanocomposites for different contents of the dopant in the raw mixture

No	Dopant, wt%	SSA, m^2/g	*d*, nm	XRD
1	–	42	44	AlN
2	Y_2O_3, 2.1	56	33	AlN, YN (tr.)
3	Y_2O_3, 3.2	63	29	AlN, YN
4	YF_3, 2.1	58	31	AlN, YN (tr.)
5	YF_3, 5.4	68	27	AlN, YN
6	Gd_2O_3, 1.5	51	35	AlN, GdN (tr.)
7	Gd_2O_3, 2.1	56	32	AlN, GdN (tr.)

The typical specific surface area and average particle size of the prepared powders are in the range of 42–68 m^2/g and 27–44 nm, respectively, depending on the content of the used dopant (Fig. 2). Increase of the dispersity of nanosized powders with the content of dopants can be explained by the change of partial pressure of components. Besides this, the presence of several components in the gas flow can inhibit growth of particles, formed at higher temperature by blocking their surface by molecules of other compounds.

Majority of particles has a hexagonal plate-like shape, characteristic for pure AlN, formed from the vapour phase (Fig. 3). The presence of separate particles with the cubic shape can be connected with the formation of YN or GdN.

Densification of AlN-Y_2O_3 (3.2 wt%) particulate nanocomposites in the SPS process starts at 1050 °C and is very intensive in the temperature range of 1100–1250 °C, reaching maximum density at 1370 °C during 2 min (Fig. 4).

Similar sintering behaviour is also characteristic of other compositions. The pure AlN sample reaches the density close to the theoretical (3.129 g/cm^3) at sintering temperature in the range of 1600–1700 °C (Table 2).

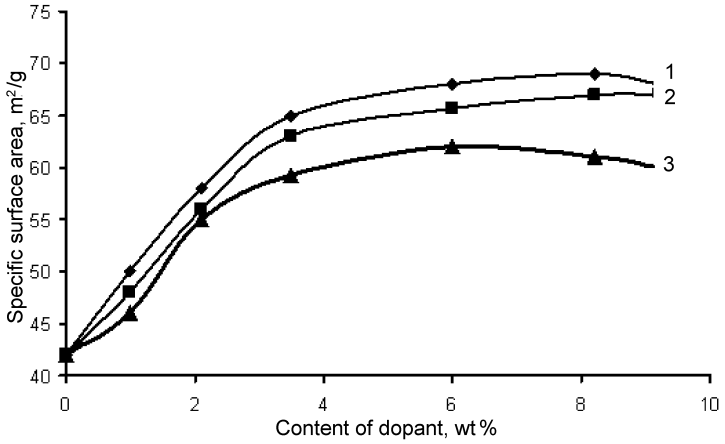

Fig. 2. Dependence of specific surface area of the produced powders on the content of dopants: 1 – YF_3; 2 – Y_2O_3; 3 – Gd_2O_3.

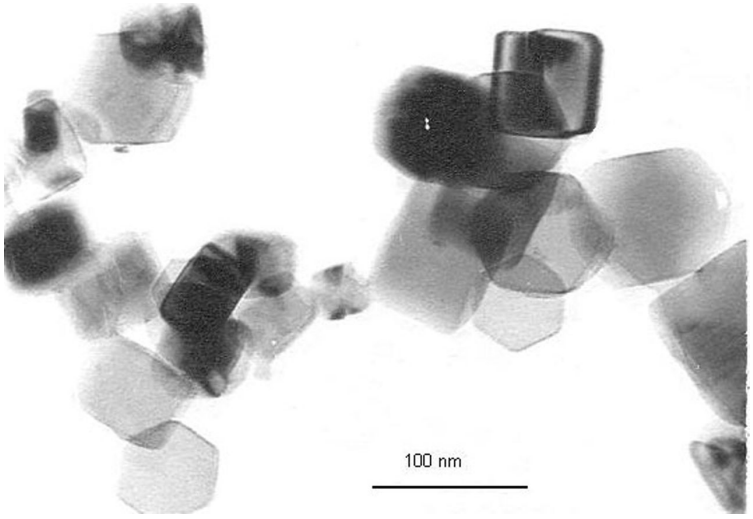

Fig. 3. Micrograph of particles prepared in the AlN-Gd_2O_3 system.

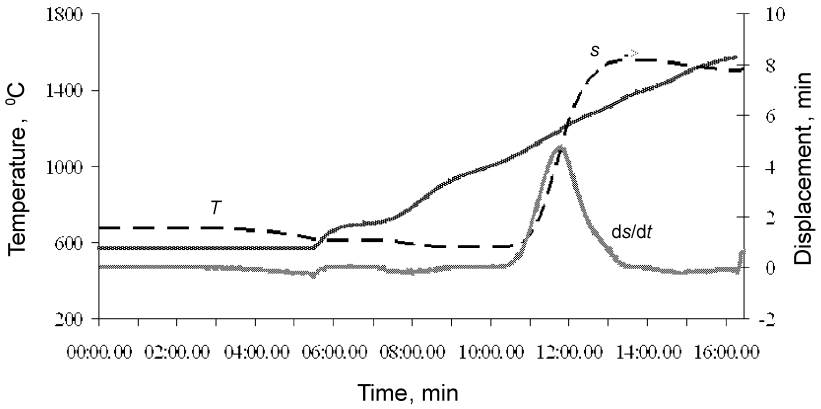

Fig. 4. Temperature (*T*), displacement (*s*) and displacement rate (d*s*/d*t*) profiles of nanosized AlN/Y_2O_3 (3.2 wt%) particulate composites during the SPS process.

Table 2. Density of sintered samples for different sintering temperatures and dopants

Temperature, °C	Density of sintered samples, g/cm^3 (dopants, wt%)				
	AlN	AlN-Y_2O_3, 3.2	AlN-YF_3, 2.1	AlN-YF_3, 3.2	AlN-Gd_2O_3, 2.1
1300	–	3.16	3.32	3.22	3.33
1400	–	3.29	3.31	3.31	3.34
1500	3.04	3.32	3.34	3.31	3.33
1600	3.11	3.31	3.30	3.32	3.34
1700	3.26	3.31	3.29	3.30	3.31

Sintering aids allow to produce dense samples at the temperature of 1300–1400 °C depending on the additive used. The obtained data show that YF_3 and Gd_2O_3 are more effective sintering aids as Y_2O_3. An increase of YF_3 content from 2.1 to 3.2 wt% has an insignificant influence on the density of the bulk material. The determined sintering temperature of AlN and AlN composites in the SPS process is 150–200 °C lower than the sintering temperature reported for nano-sized AlN-based powders, sintered by conventional pressureless sintering [9].

Literature data show that shrinkage of AlN with average particle size of 800 nm without additives in the SPS process at a pressure of 99 MPa begins at a temperature above 1100 °C and a material with relative density of 95% is obtained at 1200 °C for 50 min [8]. The different results can be explained by applied higher pressure and holding time.

According to XRD studies, the phase composition of the sintered materials differs strongly from that of powders used and it depends on additives as well as on the sintering temperature (Table 3). XRD patterns of the sintered AlN show beside aluminium nitride maxima traces of oxynitride maxima formation, which is promoted by the presence of oxygen in the raw powder. Formation of aluminium oxynitride is characteristic for AlN-Y_2O_3 and AlN-Gd_2O_3 systems, but in these systems the higher content of oxygen and presence of rare-earth elements stimulate formation of $Y_3Al_5O_{12}$ or $GdAlO_3$.

XRD patterns of sintered AlN-YF_3 system nanopowders exhibit beside AlN maxima traces of α-Al_2O_3 phase maxima and some very weak maxima at angles $2\Theta = 24.3°$, 27.5° and 31.2° of unidentified phase. There are no traces of yttria-alumina compounds (Table 3) although according to [5] sintering of AlN-YF_3 samples results in obtaining the YAG phase. Obviously, the complex phase composition of prepared by plasma chemical synthesis nanopowders in AlN-YF_3 system inhibits formation of YAG phase during SPS sintering. An interaction of AlN and alumina forms aluminium oxynitride only at 1700 °C. The traces of an unknown phase can be connected with fluorine compounds, because MicroXRF analysis confirms presence of fluorine in sintered samples (Fig. 5). On the other hand, fluorine compounds can promote formation of α-Al_2O_3.

Table 3. The phase composition of AlN composites for different sintering temperatures and used dopants

No	Dopant, wt%	Sintering temperature, °C			
		1300	1400	1600	1700
1	–	–	–	AlN, AlON	AlN, $Al_{10}N_8O_3$
2	Y_2O_3, 3.2	AlN, AlON, $Y_3Al_5O_{12}$	AlN, Al_5O_6N, $Y_3Al_5O_{12}$	AlN, Al_5O_6N, $Y_3Al_5O_{12}$	AlN, Al_5O_6N (tr.), $Y_3Al_5O_{12}$
3	YF_3, 2.1	AlN, α-Al_2O_3 (tr.)	AlN, α-Al_2O_3 (tr.)	AlN, α-Al_2O_3 (tr.)	AlN, Al_5O_6N
4	YF_3, 3.2	AlN, α-Al_2O_3 (tr.)	AlN, α-Al_2O_3 (tr.)	AlN, α-Al_2O_3 (tr.)	AlN, Al_5O_6N
5	Gd_2O_3, 2.1	AlN, $AlGdO_3$, AlO_5N (tr.)	AlN, $AlGdO_3$, AlO_5N (tr.)	AlN, $AlGdO_3$, AlO_5N (tr.)	AlN, $AlGdO_3$

The fracture microstructure of the sintered samples depends on the additives and sintering temperature (Fig. 6). The finest microstructure with grains in the range of 0.25–1.2 μm is obtained for pure AlN, sintered at 1700 °C, however, size of separate grains reaches 2.1 μm. Presence of separate large grains can be explained by the tendency of nanosized particles to form aggregates. According to [10], such aggregates determine grain size of the bulk material, manufactured by SPS process.

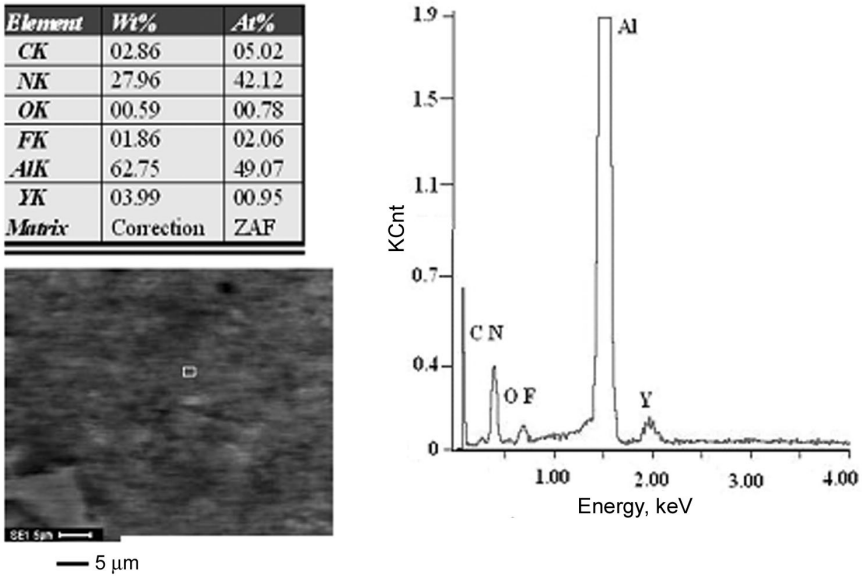

Fig. 5. Micrograph and data of micro XRF analysis of the AlN/YF_3 (2.1 wt.%) sample sintered at 1500 °C.

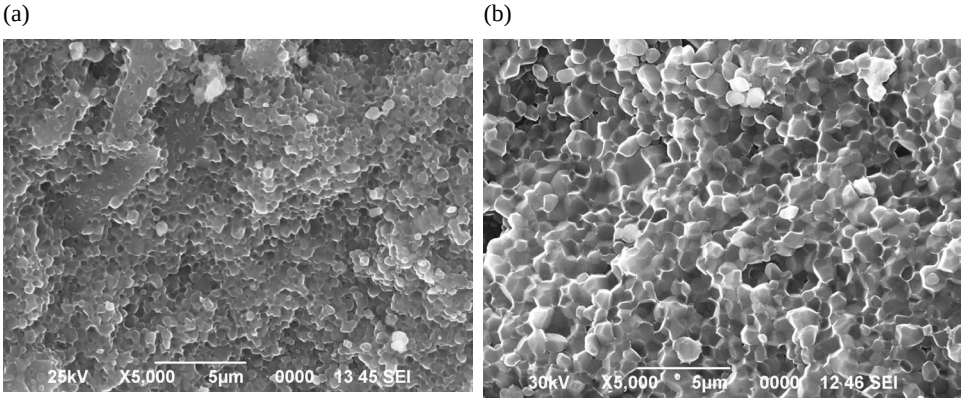

Fig. 6. Fracture microstructure of AlN (a) and AlN/Y_2O_3 (3.2 wt.%) (b) ceramics sintered at 1600 °C.

Microstructure of sintered particulate composites exhibits more coarse grains and wider grain size distribution despite lower sintering temperature, because the liquid phase promotes grain growth. The size of the biggest grains reaches 4 μm. However, the size of the majority of grains is in the range of 0.5–2.5 μm. The smallest grains have higher content of aluminium and nitrogen and lowest content of yttrium or gadolinium. An increase of the content of additives from 2.1 to 3.2 wt% leads to the formation of separate white grains with high content of yttrium or gadolinium and oxygen.

The presence of the liquid phase increases diffusivity of the components and together with formation of the secondary phases it leads to irregular distribution of elements in the sintered material.

From the obtained results follows that combining the synthesis of AlN with mixing sintering additives in thermal nitrogen plasma ensures preparation of nanosized particulate composites with good sinterability in the SPS process despite the formation of the secondary phases, but it is necessary to eliminate grain growth by minimizing the content of additives and destroying aggregates of the particles.

4. CONCLUSIONS

1. Simultaneous evaporation of aluminium and Y_2O_3, YF_3 or Gd_2O_3 additives in thermal nitrogen plasma leads to their reduction by aluminium and formation of the secondary phases –YN or GdN and X-ray amorphous phases.
2. The presence of the secondary phases reduces the AlN sintering temperature from 1700 °C to 1400 °C in the SPS process but stimulates the growth of grains.
3. The phase composition of the fabricated dense materials is determined by the used additives and sintering temperature.

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Dopeeritud AlN-nanopulbrite valmistustehnoloogia ja töötlemine

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Käesoleva töö eesmärgiks on alumiiniumnitriidi paagutatavuse parandamine, kombineerides plasmapaagutustehnoloogiat ja nanosuurusega pulberkomposiitmaterjale, mis on valmistatud samaaegsel Al- ning Y_2O_3-, Gd_2O_3- ja YF_3-lisandite aurustamisel raadiosagedusel lämmastiku plasmas. Antud lähenemine võimaldab toota kompaktseid AlN-materjale 1400 °C ja hoideaja 2 min juures, vaatamata sellele et haruldaste muldmetallide ühendid taanduvad lämmastiku plasmas ning moodustavad YN- ja GdN-faasid. Peale AlN-faasi sisaldavad valmistatud materjalid sekundaarsete faasidena alumiiniumoksünitriidi, $Y_3Al_5O_{12}$, $GdAlO_3$ või α-Al_2O_3, seda vastavalt kasutatud lisandile.