Research Article

Thermal properties of AlN polycrystals obtained by pulse plasma sintering method

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Abstract: Aluminum nitride (AlN) polycrystals were prepared by pulse plasma sintering (PPS) technique. The starting AlN powder mixtures were composed with 3.0 wt%, 5.0 wt% and 10 wt% of yttrium oxide (Y_2O_3), respectively. Relative density of each polycrystal was measured by hydrostatic method and evaluated higher than 97%. X-ray diffraction (XRD) method was used for phase examination of the samples after heat treatment. Microstructure examination supported by computer-aided analysis was performed by scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). The results were correlated with thermal conductivity of the samples carried out by laser pulse method (LFA). The influence of the rapid sintering technique and yttrium oxide additive content on the thermal conductivity and microstructure appearance of AlN polycrystals was clearly shown.

Keywords: aluminum nitride (AlN); thermal conductivity; microstructure; thermal diffusivity; specific heat

1 Introduction

Aluminum nitride (AlN) is considered as a challenging material for structural and functional applications, because it has a very high thermal conductivity among other ceramic compounds. In the form of monocrystal or polycrystal, AlN is used in electronic devices, thus squeezing out conventional materials like SiO_2, Al_2O_3 or BeO, which are harmful for human body [1,2]. AlN is applied for sensors and heat exchangers to improve their sensitivity and efficiency [3]. Due to its thermal properties, it is also used in arms industry as a part of high-power and high-resolution radars [4]. The thermal conductivity (λ) of polycrystalline AlN mainly depends on the level of oxygen content dissolved in the crystallographic structure, microstructure appearance and nature of points and linear defects. These factors can radically reduce λ from 320 W/(m·K) to 70 W/(m·K) [5] unless they are controlled well at every stage of manufacturing procedure [6]. Preparation of dense AlN polycrystals requires the addition of liquid phases for sintering. Commercially, MgO, CaO or rare-earth metal oxides are used, but the most promising addition is yttrium oxide (Y_2O_3) resulting in the highest value of thermal conductivity. AlN grains are usually covered by thin layers of alumina (Al_2O_3); therefore, during sintering, yttrium oxide forms several compounds with alumina, e.g., YAP ($YAlO_3$), YAG ($Y_3Al_5O_{12}$) and YAM ($Y_4Al_2O_9$). The garnet formation

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promotes densification process but additionally leads to the removal of oxygen from AlN structure at temperatures above 1750 ℃ [7]. This is related to improving thermal conductivity and density of the polycrystals. The introduction of liquid phases is associated with grain growth and decreasing in concentration of grain boundaries to improve thermal properties [8]. An effective method of preparation AlN polycrystals having higher λ is pressureless sintering; however, it needs a long time of heat treatment, usually 2 h at 1800 ℃ [9,10].

The aim of this study is to obtain AlN samples by a rapid densification process—pulse plasma sintering (PPS, modification of SPS (spark plasma sintering)). The literature about such preparation of AlN polycrystals is rather limited. Therefore, the results given below fulfill this gap and make good starting points for further scientific discussion.

2 Materials and methods

To produce AlN sinters, commercially available AlN powders (H.C. Starck GmbH, Germany) were used. The powder morphology observed by scanning electron microscopy (SEM, Nova NANOSEM 200 from FEI), and grain size distribution measured with laser diffraction method in alcohol environment (Mastersizer 2000 of Melvern Intruments) are shown in Figs. 1 and 2, respectively. It is detected that the average size of grains is 1.7 μm, which confirms D_{50} in the range of 0.8–1.8 μm taken from the company's analysis. Yttrium oxide produced by the same company having medium-sized grains of 0.8 μm was added to prepare mixtures for sintering.
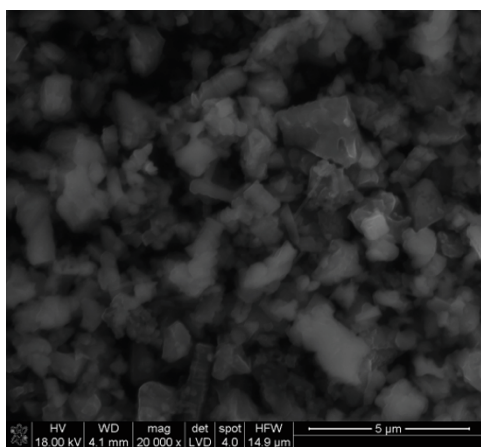

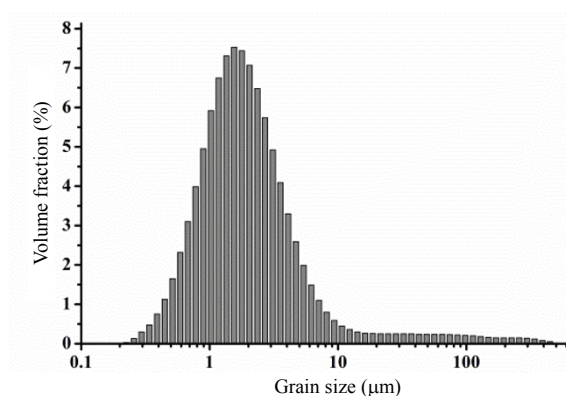Fig. 1   Morphology of commercial AlN powders.

Fig. 2   Grain size distribution of commercial AlN powders.

AlN powders were mixed with 3.0 wt%, 5.0 wt% and 10 wt% of Y_2O_3. The mixtures were homogenized in isopropyl for 24 h by silicon nitride grinding media. The as-prepared powders were granulated and compacted in carbon mould, and then sintered by PPS in nitrogen flow [11]. The heating rate of 170 ℃/min was associated with the pressure of 81 MPa. The maximum temperature of 1500 ℃ was dwelled for 600 s. The apparent density of the sintered AlN was measured using hydrostatic method, and compared to the theoretical density calculated on the base of X-ray diffraction (XRD) analysis. The phase composition of AlN polycrystals was qualitatively and quantitatively examined by XRD method. The thermal measurements were performed by Netzsch LFA 427 apparatus. The thermal diffusivity and specific heat were determined by laser pulse method (LFA) at temperatures from 25 ℃ to 600 ℃ in step of 100 ℃ in argon flow with "Cape–Lehmann + pulse correction" computational model. The thermal expansion coefficient was measured by a Netzsch DIL 402C dilatometer at temperature range from 20 ℃ to 600 ℃. The thermal conductivity was calculated on the base of the above measured thermal properties. All the samples were polished and then mechano-chemically etched to reveal microstructure details. Microstructure observation was performed by SEM. The grain size of the sintered materials was estimated on SEM images with computer-aided analysis—Aphelion Image Processing Programme.

3 Results and discussion

The relative density and phase composition of AlN

polycrystals are summarized in Table 1. All the samples' relative densities exceed 97%, and two phases are detected in the XRD patterns, i.e., AlN and Y_2O_3 garnets. Increasing quantity of Y_2O_3 in starting mixtures leads to higher concentration of YAP and YAM phases. Reaction between Al_2O_3 originated from grain surface and Y_2O_3 leads to the formation of garnets during sintering. It is associated with the decreasing concentration of oxygen in AlN structure resulting in higher thermal conductivity of the obtained polycrystals. It is shown that a short time of heat treatment, e.g., 600 s, and low temperature are enough to prepare full dense AlN polycrystals by PPS technique.

LFA-measured values of specific heat, thermal diffusivity and thermal conductivity of the polycrystals are collected in Table 2. The highest λ is achieved for the samples with 5 wt% of yttrium oxide. All the polycrystals have rather good thermal conductivity ranging from 78 W/(m·K) to 100 W/(m·K) at 25 ℃. However, these results are not as high as those of pressureless sintered AlN [10,12]. This is due to a very fine microstructure of the obtained samples and high concentration of intergranular boundaries. Other concentrations of yttrium oxide dopant (3 wt% and 10 wt%) cause lower thermal conductivity. In the case for 3 wt% of yttrium oxide addition, AlN structure contaminated by oxygen is a plausible cause of lower thermal conductivity. On the other hand, the increased porosity of AlN polycrystals sintered with 10 wt% of yttrium oxide is a reason of lower λ compared to 5 wt% of yttrium oxide content.

Table 1   Relative density and phase composition of polycrystalline AlN

Y_2O_3 addition (wt%)	Apparent density (%)	Phase composition (wt%)				
		AlN	YAG	YAP	YAM	Gamma AlON
3.0	99.9	94.5	5.0	—	—	0.5
5.0	97.9	91.2	5.8	3.0	—	—
10	97.2	87.1	—	6.3	6.6	—

Table 2   Thermal properties of AlN sinters with various additions of yttrium oxide

Temperature (℃)	Thermal diffusivity (mm²/s)			Specific heat (J/(g·K))			Thermal conductivity (W/(m·K))		
	3 wt%	5 wt%	10 wt%	3 wt%	5 wt%	10 wt%	3 wt%	5 wt%	10 wt%
25	27.9	31.7	30.7	0.84	0.94	0.92	78.8	100.1	93.8
100	22.3	25.0	24.2	0.99	1.14	1.10	71.1	93.5	87.1
200	17.8	19.0	18.7	1.10	1.24	1.19	65.3	81.5	76.5
300	14.8	15.8	15.3	1.32	1.49	1.43	61.6	72.1	67.5
400	12.8	13.5	13.0	1.28	1.45	1.39	59.6	64.8	60.1
600	10.0	10.5	10.1	1.33	1.52	1.46	56.6	53.3	49.4

For the obtained sinters, thermal expansion coefficients (CTE) are measured. CTE values for the temperature range of 40–600 ℃, are estimated to 5.72×10^{-6} (℃)$^{-1}$, 5.41×10^{-6} (℃)$^{-1}$ and 5.54×10^{-6} (℃)$^{-1}$ with 3 wt%, 5 wt% and 10 wt% Y_2O_3, respectively. The various additions of sintering aid do not influence significantly on thermal expansion of AlN. These results are similar to the literature data [13].

The microstructure appearance of AlN samples are shown in Figs. 3–5. They are very similar in shape of grains for each content of yttrium oxide dopant. Two phases are clearly visible. The grey fields are corresponded to pure AlN grains and light spots are attributed to yttrium-containing phases. EDS examination shown in Fig. 3 and XRD analysis indicate the formation of YAG at grain boundary for the sample containing 3 wt% of yttrium oxide dopant. It can be concluded that a short time of rapid densification by PPS gives good crystallized garnet phase located at grain boundary. This phase is distributed uniformly at all images shown in Figs. 3–5.
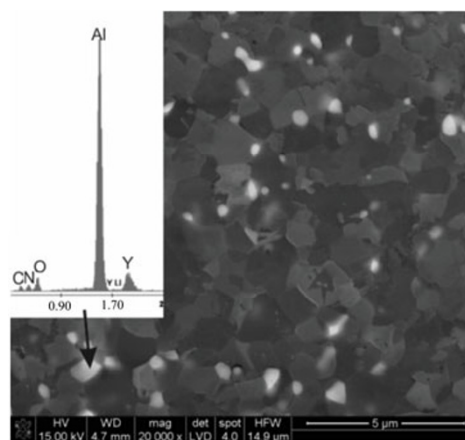

Fig. 3   Microstructure of sintered AlN polycrystals (3 wt% Y_2O_3, sintered at 1500 ℃ for 600 s).
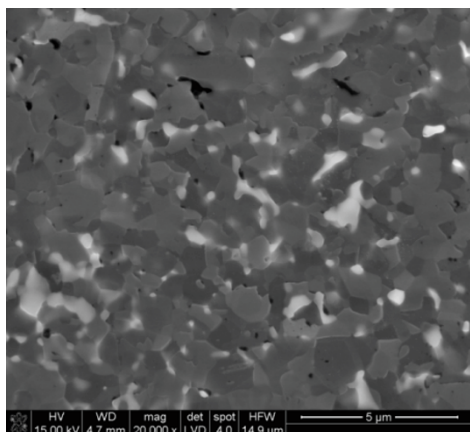
Fig. 4   Microstructure of sintered AlN polycrystals (5 wt% Y_2O_3, sintered at 1500 ℃ for 600 s).
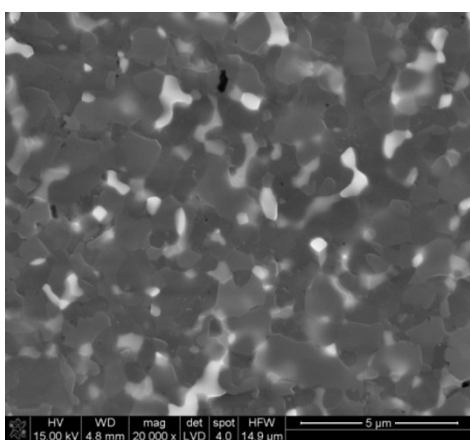

Fig. 5   Microstructure of sintered AlN polycrystals (10 wt% Y_2O_3, sintered at 1500 ℃ for 600 s).

polycrystals described in the present work were prepared at lower temperature of about 250 ℃.
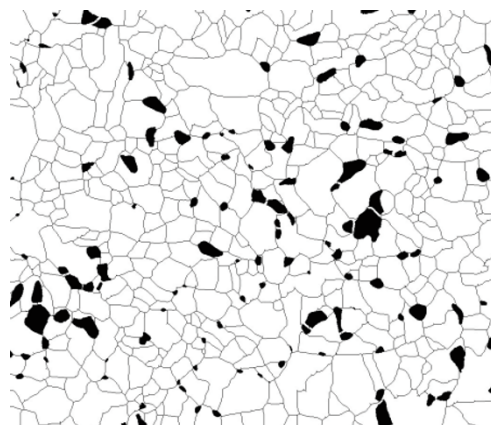

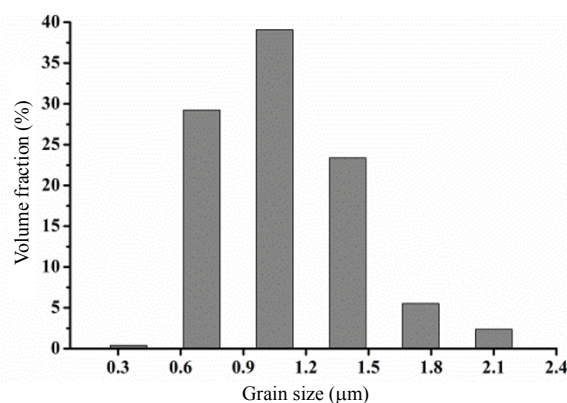Fig. 6   Binary microstructure image of sintered AlN polycrystals (5 wt% Y_2O_3, sintered at 1500 ℃ for 600 s).

Fig. 7   Grain size distribution of sintered AlN polycrystals (5 wt% Y_2O_3, sintered at 1500 ℃ for 600 s).

To calculate grain size distribution, the image shown in Fig. 4 is binarized (Fig. 6) and then examined by computer-aided analysis. 40% of the grains have an average grain size estimated to 1.0 μm as shown in Fig. 7. This value is similar to that of the initial powders, and thus it is concluded that grain growth does not occur during PPS process significantly. For other microstructures, the results are very similar; thus we believe that the amount of yttrium oxide dopant does not control AlN microstructure appearance sintered by PPS. The difference in thermal conductivity of the samples can be explained by porosity changes or specific YAG, YAM or YAP formation. This reaction can reduce the oxygen content inside AlN grains, and therefore each sample has different thermal conductivity. The obtained thermal results for lower temperature sintered polycrystals (PPS) are similar to SPS-sintered materials [14], whose authors used maximum 3 wt% various additive mixtures (Sn_2O_3–Li_2O–Y_2O_3). However, AlN

4   Conclusions

It is possible to obtain dense polycrystals of AlN by PPS method at temperature of 1500 ℃ in a very short time. The obtained AlN polycrystals are characterized with high density (above 97%) and good thermal properties. All the samples have fine microstructure with grain size estimated to 1.0 μm, which can have an influence on the mechanical property improvement. The thermal conductivity of AlN sinters is comparable to polycrystals prepared by SPS method.

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