J Mater Sci (2006) 41:7934–7938
DOI 10.1007/s10853-006-0862-5

Microstructure and properties of spark plasma sintered AlN ceramics

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Received: 4 July 2005 / Accepted: 18 November 2005 / Published online: 22 September 2006

Abstract Spark plasma sintering (SPS) is a newly developed technique that enables poorly sinterable aluminum nitride (AlN) powder to be fully densified. It is addressed that pure AlN sintered by SPS has relatively low thermal conductivity. In this work, SPS of AlN ceramic was carried out with Y_2O_3, Sm_2O_3 and Li_2O as sintering aids. Effects of additives on AlN densification, microstructure and properties were investigated. Addition of sintering aids accelerated the densification, lowered AlN sintering temperature and was advantageous to improve properties of AlN ceramic. Thermal conductivity and strength were found to be greatly improved with the present of Sm_2O_3 as sintering additive, with a thermal conductivity value about 131 $Wm^{-1}K^{-1}$ and bending strength about 330 MPa for the 2 wt% Sm_2O_3-doped AlN sample SPS at 1,780 °C for 5 min. XRD measurement revealed that additives had no obvious effect on the AlN lattice parameters. Observation by SEM showed that AlN ceramics prepared by SPS method manifested quite homogeneous microstructure. However, AlN grain sizes and shapes, location of secondary phases varied with the additives. The thermal conductivity of AlN ceramics was mainly affected by the additives through their effects on the growth of AlN grain and the location of liquid phases.

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Introduction

Aluminum nitride (AlN) ceramic has a number of attractive properties for applications as substrate and package material in microelectronic devices, including its high thermal conductivity and electric resistivity, low dielectric constant and thermal expansion coefficient close to that of silicon (Si). However, AlN ceramic is difficult to sinter due to the slow sintering process and the requirement of extremely high sintering temperature. Rare and/or alkaline earth oxides (Y_2O_3, Dy_2O_3, CaO, etc.) were used as sintering aids to reduce sintering temperature and accelerate the sintering processes. But their effects were limited [1]. In recent years, it has been found that ceramic powders can be densified at a relatively low temperature and in a very short time through spark plasma sintering (SPS) technique [2]. For non-conductive ceramic powders, heating occurred through heat transfer from the graphite die and punches in the SPS process [3]. With the application of pulsed direct current, thermal and electric breakdown phenomena were most likely to occur at high temperature and skin current could be formed on powder surface. Plasma was generated, and consequently it engendered concentrated heating in the sinter and accelerated the diffusion and contact of ceramic particles' surfaces, as Omori figured [4]. Zhang

[5] advanced the sintering mechanism by the deflection of pulse electric current flowing from punches to die generated thermal effect engendered by electromagnetic field and secondary electromagnetic wave in the die lacuna. The thermal effect could accelerate the densification process tremendously. Qiao et al. reported [6] that AlN ceramic with a relative density of 99.5% could be achieved by SPS at a relatively low temperature of 1,600 °C without any sinter aid. However, the thermal conductivity of AlN sample sintered by SPS was only 41 and 56 W/m K, though the samples were almost fully densified and held a clean grain boundary. Qiao believed that the small grain size in the AlN sample sintered by SPS was the main controlling factor of thermal conduction. Khor et al. studied the thermal conductivity of AlN samples doped CaF_2 [7] or Sm_2O_3 [8], and compared them with pure AlN. Results indicate that sintering aids are beneficial to improve the thermal conductivity of AlN samples. They obtained AlN ceramic with 129 and 118 W/m K thermal conductivity through SPS. It was well acknowledged that the amount of oxygen-related defects in AlN lattice and distribution of the secondary phase in grain boundary were all important factors as well as grain size [9, 10]. Addition of rare or/and alkaline earth oxides into AlN sinter is a virtual measure to restrain the diffusion of oxygen. Different additives, however, brought different effects on microstructure and properties of AlN materials [11, 12]. Thus, additives for AlN with perfect properties must be chosen and validated elaborately in a variety of preparation process. The effects of additives on microstructure and properties of AlN ceramics prepared by conventional sintering processes were reported frequently [13]. Comparatively, study on the effects of sintering aids on properties of AlN ceramics fabricated by SPS was rather few.

In the present work, commercial AlN powder was sintered by SPS at different temperature and with Sm_2O_3, Y_2O_3 and Li_2O as sintering aids. The effects of additives on the densification and microstructure of AlN ceramics were investigated, and the properties affected by the relative microstructure were also studied.

Experimental procedure

Commercially available AlN powder (Fujian Sinocera Advanced Materials CO. Ltd., grade I, average diameter is 2.0 μm), Sm_2O_3 (purity is 99.9%), Y_2O_3 (purity is 99.99%) and Li_2CO_3 (analytically pure) were dispersed in absolute alcohol through ultrasonic and mechanical agitation. Table 1 showed the proportion of mixtures. The slurry was dried in a vacuum oven. After mixing and drying, the mixture was ground and then sintered by SPS at a uniaxial pressure on the die and under a N_2 gas pressure of 0.07 MPa. The pressure applied to the AlN powder was kept constant at 25 MPa during sintering. Density of samples was measured by Archimedes displacement method with distilled water as the immersion medium, and relative density was calculated through the theoretic density of raw materials regardless of the effect of generation of aluminate. AlN lattice parameters were identified by X-ray diffraction (XRD, D/Max-IIIA, Rigaku, Japan) according to internal standard method with monocrystalline silicon as a reference compound. Microstructure was observed by scanning electrons microscopy (SEM, SX-40, Akashi Seisakushu, Japan). Thermal conductivity of samples was measured by a laser-flash technique (TC-7000 Laser Flash Thermal Constant Analyzer, Japan).

Results and discussions

There were two heating stages in SPS sintering process of powders. The heating rate and the dwell time at sintering temperature was 200 °C/min and 5 min respectively. Fig. 1 illustrates the *Z*-axis displacement of lower punch of SPS system during the heating process of various powders. The displacement was not the actual expansion–shrinkage of samples, but it could reflect the initial sintering temperature and densification procedure of AlN powders. At the beginning of the heating process, all samples experienced an expansion. Then, samples began to shrink at certain temperature. The temperature, as for AlN powder, was about 1,500 °C, while it was about 1,380 °C for specimen 4 and 1,240 °C for specimen 2 and specimen 3 powder. These temperatures were the initial sintering temperature of the samples. These results indicated that all aids used in our research were beneficial to lower the sintering temperature and promote the densification of AlN ceramics, and binary aids were more effective than single aid.

Table 1 Mixture's dosage of powders

Sample	AlN (wt%)	Sm_2O_3 (wt%)	Y_2O_3 (wt%)	Li_2CO_3 (wt%)
1 AlN	100			
2 AlN–Sm_2O_3–Y_2O_3	97	1.5	1.5	
3 AlN–Sm_2O_3–Li_2O	97.5	1.5		2.45 (1 wt%Li_2O)
4 AlN–Sm_2O_3	98	2		

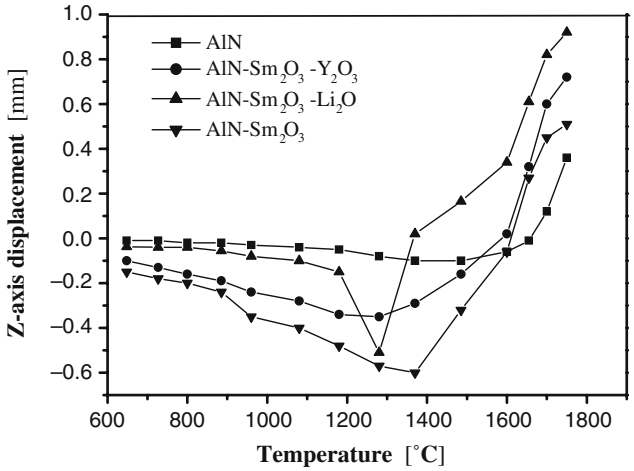

Fig. 1 *Z*-axis displacement of AlN powders in SPS sintering

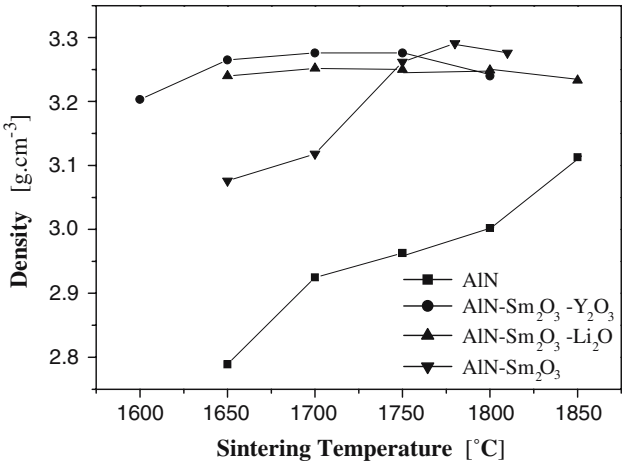

Fig. 2 Relative density of AlN specimen sintered at different temperature

Figure 2 shows the density of AlN specimens sintered at different temperature. In this work, the sinter density of pure AlN powder reached 3.113 g/cm^3 (95% of theoretical density) sintered at 1,850 °C. With the aid of oxides, the initial sintering temperature of AlN powders was reduced, and the density of sinters was higher than pure AlN sinter obviously. The above-mentioned results proved that additives were useful for densification of AlN ceramics. It was unforeseen that the highest densities of AlN sinter with binary additives were lower than that with single Sm_2O_3. This was regarded that the AlN densification significantly related to the characteristics of SPS technique. Binary additives caused the liquid phase appearing at a lower temperature and the amount of liquid increasing. Meanwhile, in the SPS process, the sintering time was quite short and the gas remained between the original particles or generated during the sintering had not enough time to escape from the sinter. This resulted in porous sample and low density.

Table 2 presented the characteristics of AlN specimens with highest density sintered with additives. Their thermal conductivity was distributed in the range of 93~131 W/m K and bending strength of 261~330 MPa. These data indicated that properties of the AlN samples were affected by additives markedly.

Except for pure AlN, the relative densities of samples were similar. So the difference of thermal conductivities was not mainly caused by the difference of the densities of samples doped additives. It is well acknowledged that oxygen dissolving into AlN lattice during the sintering process can form oxygen-related defects in the lattice. Slack [14] and Harris et al. [15] supported their model of the oxygen-related defects in AlN with the results of XRD lattice parameter measurements. This means that lattice parameters will change with the oxygen concentration in AlN. For the samples in Table 2, Fig. 3 showed their AlN unit cell volumes and room-temperature thermal conductivity. The AlN unit cell volumes of four samples had only some variation and were in range of 41.749×10^{-3}~41.767×10^{-3} nm^3. The relationship between cell volumes and thermal conductivity was not notable in our work. These results implied probably that these sintering aids had no obvious effect on the oxygen content in the AlN lattice of spark plasma sintered AlN. Thermal conductivity of these samples should be affected by their microstructure together with other factors.

SEM images of fracture surfaces of sintered AlN specimens were shown in Fig. 4. In back-scattered electron images, the phase in grey was AlN grains and the white part was liquid phases, or called secondary

Table 2 Properties of different AlN specimens

Sample	Sintering condition	Density (g cm^{-3})	Relative density (%)	Thermal diffusivity (cm^2 s^{-1})	Thermal conductivity (W m^{-1} K^{-1})	Bending strength (MPa)
AlN	1,850 °C, 5 min	3.11	95.0		66	
AlN–Sm_2O_3–Y_2O_3	1,750 °C, 5 min	3.27	98.6	0.432	113	303.2 ± 18.5
AlN–Sm_2O_3–Li_2O	1,750 °C 5 min	3.25	98.5	0.363	93	261.2 ± 14.0
AlN–Sm_2O_3	1,780 °C, 5 min	3.29	99.4	0.504	131	330.3 ± 25.7

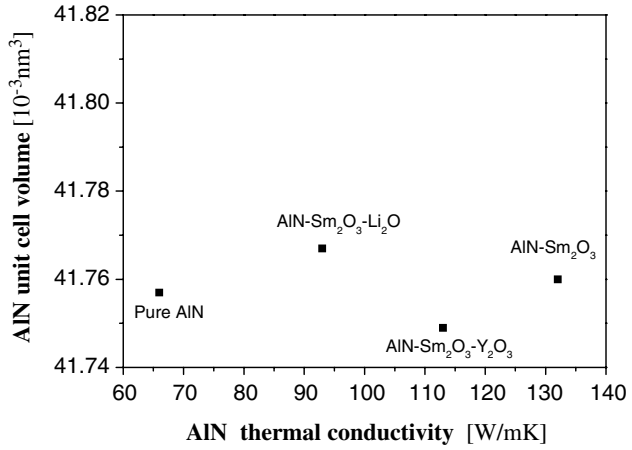

Fig. 3 AlN unit cell volume and thermal conductivity of AlN samples

phases. It was observed that the AlN grains were polyhedral and grew homogeneously in the sample adding Sm_2O_3, which were different from the irregular grain shape in AlN–Sm_2O_3–Y_2O_3 and AlN–Sm_2O_3–Li_2O samples. In addition, the distribution of liquid phases in various samples was very different, this could be surveyed obviously in the back-scattered images. In the sample adding Li_2CO_3, liquid phase spread adequately along the AlN grain boundaries, and AlN grains were separated by the secondary phase. Comparatively, the secondary phase in AlN–Sm_2O_3–Y_2O_3 sample was located at the triple points of AlN grain or two-grain junctions, and in AlN–Sm_2O_3 sample, the secondary phase was limited and AlN grains contacted to each other. The phenomena showed that the wettability of AlN grains and aluminates formed by Al_2O_3 and additives differed from the samples with various sintering aids. The wettability of aluminate contained Li_2O with AlN grain was better than Sm–Y–Al–O and Sm–Al–O eutectic compounds. Grain sizes in the three samples were different too. In AlN–Sm_2O_3–Y_2O_3 sample, the grain size was bigger in some sort. There were some singularly big grains in the AlN–Sm_2O_3–Li_2O sample. The microstructure of AlN–Sm_2O_3 sample was more homogeneous than of other samples. In general, densification, grain size and the distribution of secondary phase play important roles on the thermal conductivity of AlN ceramics. The scattering of phonon was enhanced if grain size was small and AlN grains were separated from each other. This induced the deterioration of thermal conductivity of AlN ceramics. Therefore, the highest thermal conductivity belonged to the AlN–Sm_2O_3 sample and the thermal conductivity of the AlN–Sm_2O_3–Li_2O sample was lower than that of other samples in our work. It had some discrepancy with the result [12] that the addition of Li_2O was beneficial to improve thermal conductivity of AlN sintered by atmospheric sintering.

Conclusions

Dense AlN ceramics can be achieved by SPS at a lower sintering temperature and in a shorter time with sintering aid Y_2O_3, Sm_2O_3 and Li_2O. Additives lower the sintering temperature of AlN ceramics and accelerate their densification by formation liquid phases in the samples. Result of XRD measurements indicates that AlN unit cell volumes have no obvious difference from samples with different sintering aids. This is thought that additives have no distinct effect on the oxygen

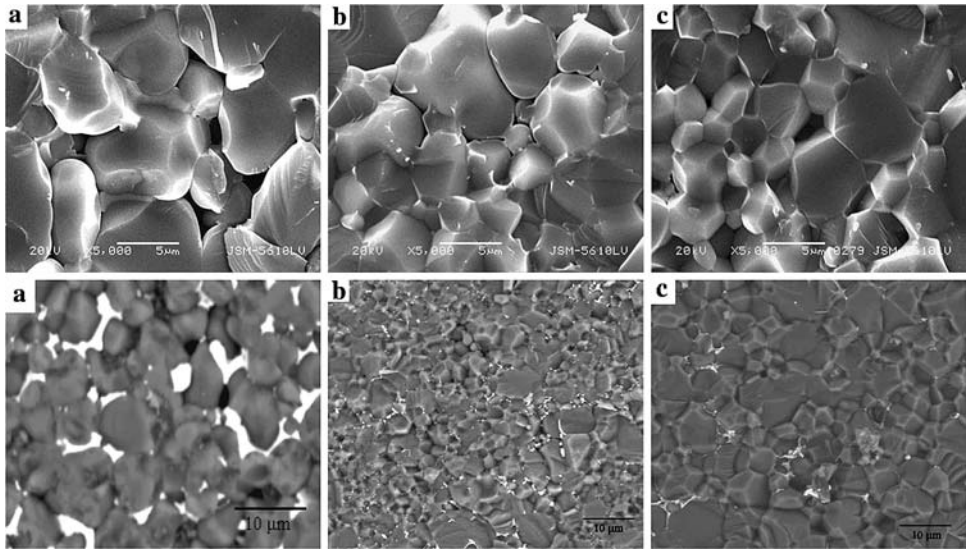

Fig. 4 Secondary electron and back-scattered electron images of fracture surfaces of sintered AlN specimens by SEM (**a**) AlN–Sm_2O_3–Y_2O_3, (**b**) AlN–Sm_2O_3–Li_2O, (**c**) AlN–Sm_2O_3

concentration in AlN lattices for SPS sintered AlN, because SPS process completes in very short time. However, additives affect the microstructure of AlN samples in grain size, grain shape and location of secondary phase. Compared with the AlN–Sm_2O_3–Li_2O and AlN–Sm_2O_3–Y_2O_3 samples, the sample with 2% Sm_2O_3 manifests a more homogeneous microstructure, and AlN grain shape in the sample is regular polyhedron. It exhibits better mechanical properties and higher thermal conductivity as well.

Acknowledgements This work was supported by National Natural Science Foundation of China (50232020).

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