

Preparation and characterization of Al/AlN composites sintered under high pressure

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Abstract High-density aluminium/aluminium nitride (Al/AlN) composites were obtained by high pressure sintering method under 3.0–5.5 GPa and 860–1,690 °C for only 20–70 min. The results show that the relative density of Al/AlN composite containing 40 wt.% Al can reach 99.37% under 5.0 GPa and 1,600 °C for only 20 min. This sintering time is quite shorter than conventional methods (1–6 h). The fracture surfaces show homogeneous microstructure and transcrystalline fractures are easy to find.

Introduction

AlN has attracted much attention for some excellent properties, such as high thermal conductivity, good mechanical strength, low-density value, a low thermal

expansion coefficient and no reaction with aluminum. So AlN is attractive for applications in metal handing, as heat sinks, in semiconductor devices and electronic substrates, and as grinding media, seals, filler materials, etc. [1–3]. In general, the intrinsic thermal conductivity of AlN is $320 \text{ Wm}^{-1} \text{ K}^{-1}$. However, in practice, the thermal conductivity varies from about $80\text{--}260 \text{ Wm}^{-1} \text{ K}^{-1}$ [4, 5]. The thermal expansion coefficient of AlN is $4.5 \times 10^{-6} \text{ K}^{-1}$ and it's similar to Si, which makes it possible for application as electronic substrates [6].

However, as in the case of other ceramic materials, pure AlN shows brittle property as its intrinsic defect, which confines its applications. To improve the mechanical and thermomechanical properties of AlN, many attempts have been made by adding a dispersed second phase in the ceramic matrix. One of the important ways is the addition of metal phase with high mechanical and thermal properties. Several formation methods of aluminium/aluminium nitride (Al/AlN) composites have been reported, including directed growth reaction, pressureless liquid metal infiltration, nitrogen plasma-alloy reaction and spray deposition, and pressure metal infiltration [7–14]. In order to manufacture composites with superior density, high pressure sintering method could be an alternative for Al/AlN composites. This method provides a seal environment for samples sintering and reduces the request of sintering temperature and time.

In this work, high-density Al/AlN composite was obtained by high pressure sintering (3.0–5.5 GPa). The effects of pressure, sintering time and temperature on the sintering property were studied. The results show that relative density can reach more than 99% in a shorter sintering time (20 min) and at a lower temperature (about 1,500 °C) compared with conventional methods (1–6 h, above 1,700 °C) [5, 6, 15].

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Experimental procedure

Preparation

Original AlN powder (produced by SHS method) was the commercial product from Antai Company in Beijing. The principal elements of this powder are presented in Table 1. The element of O is the main impurity in the form of Al₂O₃ covered on the surface of AlN grains. Figure 1a is the scanning electron micrograph (SEM) of AlN powder, it can be seen that the particles are not regular in shape, some are in the shape of board and a few agglomerates are observed in some areas. The size of the majority particles varies from 0.5 to 5 μm, and the average particle size is 2.6 μm.

Commercial Al powder was supplied by Xizhong Company in Beijing, with the purity more than 99.5%. Figure 1b presents the morphology of powder particles. Most of the particles are in the shape of ball or ellipse and not regular either. Its size varies from 10 to 70 μm, and the average size is 44.5 μm. The same to the AlN powder, agglomeration phenomenon exists also in Al powder.

The raw material mixtures were mixed in ethanol for 4 h in order to gain homogeneous mixtures. After drying in vacuum box, samples of each composite were pre-pressed by uniaxial pressing under 100 MPa. The pre-pressed samples were 8 mm in diameter and 5 mm in thickness.

The sintering of composites was performed in a cubic anvil high pressure and high temperature (HPHT) apparatus (China type, SPD-6 × 1200) (Fig. 2) with a cubic assembly block of 37.5 mm edge length (Fig. 3). The heater was graphite tube whose inner walls were coated with insulation material to avoid interaction between the sample and insulated tube and also to facilitate the demoulding process. This method could resist the outer influence just like oxidation.

Characterization

After being sintered, samples were polished to wipe off the impurities on the surfaces. The phases were characterized by X-ray diffraction (XRD) with Cu K_α radiation. And the fracture surfaces of samples were observed under SEM. The density was measured by the Archimedes principle and relative density was calculated by theoretical density of Al/AlN composite.

Table 1 Element composition of AlN powder

Element	Al	N	O	Fe	C
wt.%	>65.0	>33.1	<0.90	<0.015	<0.06

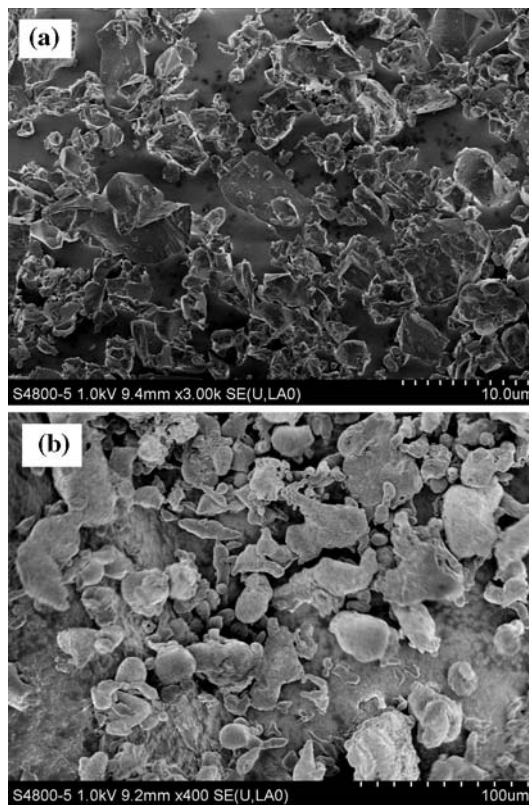


Fig. 1 SEM micrographs of the raw material powder (a) AlN and (b) Al

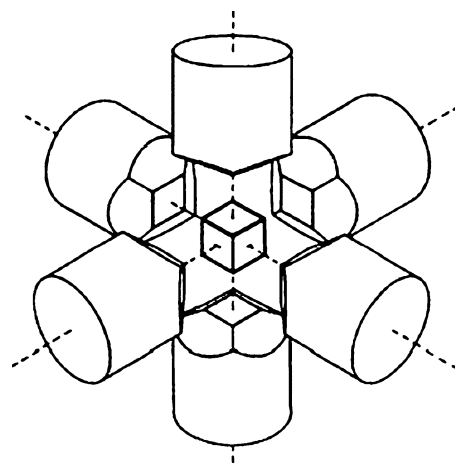


Fig. 2 Schematic diagram of a sintering cell in HPHT apparatus (China type, SPD-6 × 1200)

Results and discussion

XRD analysis

Figure 4 is XRD patterns of (a) AlN, (b) Al powder and (c) Al/AlN composite containing 20 wt.% Al sintered at 1,600 °C and 4.5 GPa for 50 min. No extra peaks are

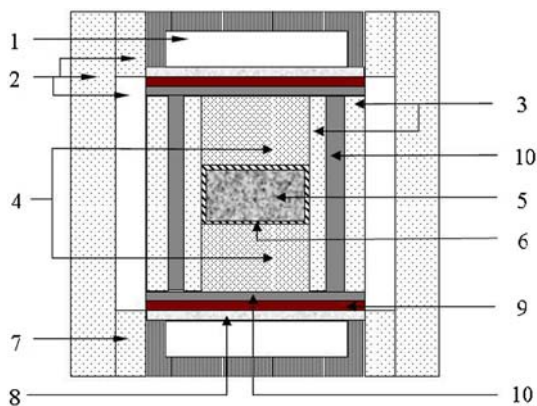


Fig. 3 Sample assembly for Al/AlN composite. 1: steel ring; 2: pyrophyllite block; 3: insulated tube; 4: insulated column; 5: sample; 6: insulation material; 7: pyrophyllite ring; 8: steel plate; 9: copper plate; 10: graphite heater

found except those attribute to AlN and Al. This proves that AlN is indecomposable at 1,600 °C and high pressure (4.5 GPa). The calculated lattice parameters of AlN based on X-ray data in Fig. 4c are $a = 3.112$, $c = 4.975$. These values are slightly smaller than those calculated from the X-ray data of AlN raw material powder, which are $a = 3.115$, $c = 4.984$. The reason for the small contraction (about 0.1%) of the lattice parameters mainly results from the high-pressure treatment. Pressure allows a modification of the interatomic distances and thus makes the lattice parameters decrease. This conclusion is in agreement with N. P. Bezhenar, M. Ueno and A. Onodera [16, 17], where the lattice parameters of AlN decreased by 0.1–0.13% after high pressure sintering (8 GPa).

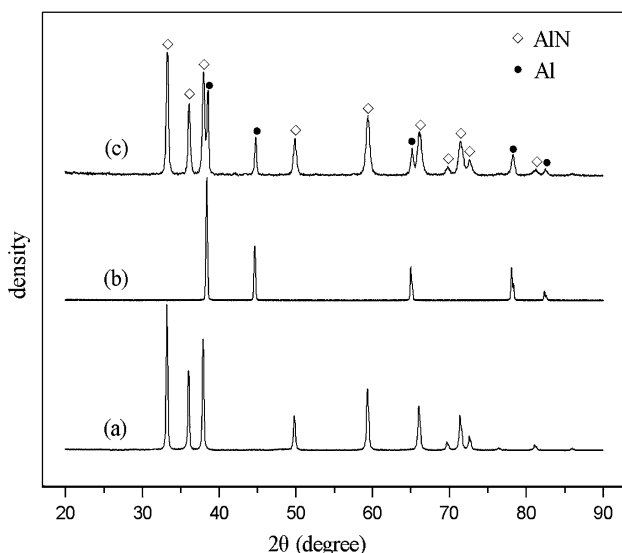


Fig. 4 XRD pattern of (a) AlN (b) Al powder and composite (20 wt.% Al) sintered at 1,600 °C and 4.5 GPa for 50 min

Sintering property

Figures 5–7 give the relative density as a function of sintering time, temperature, pressure, respectively. The respective sintering conditions have shown in figures.

As shown in Fig. 5, the relative density can reach highly up to 99.37% for only 20 min, we have not found other sintering methods can reach this level for such a short time so far. From 20 to 40 min, the relative density increases to 99.89%. But after 40 min, the relative density value is basically invariable. Obviously, 40 min is the optimal sintering time for the Al/AlN composites containing 40 wt.% Al at 1,600 °C and 5.0 GPa. From above analysis, it can be concluded that density increase mainly happens in

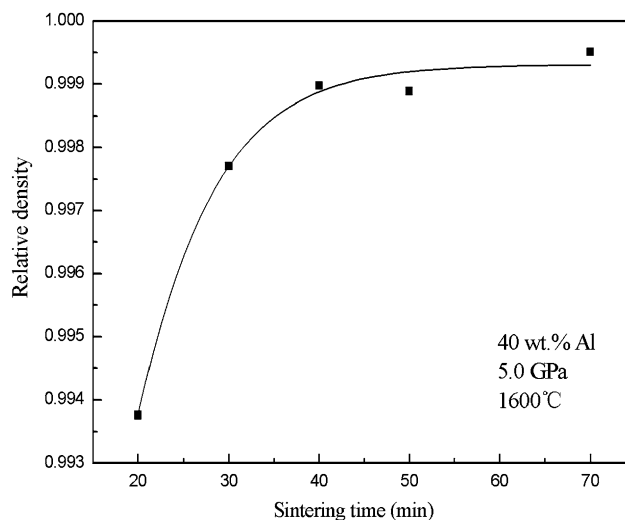


Fig. 5 Effects of sintering time on relative density of Al/AlN composites

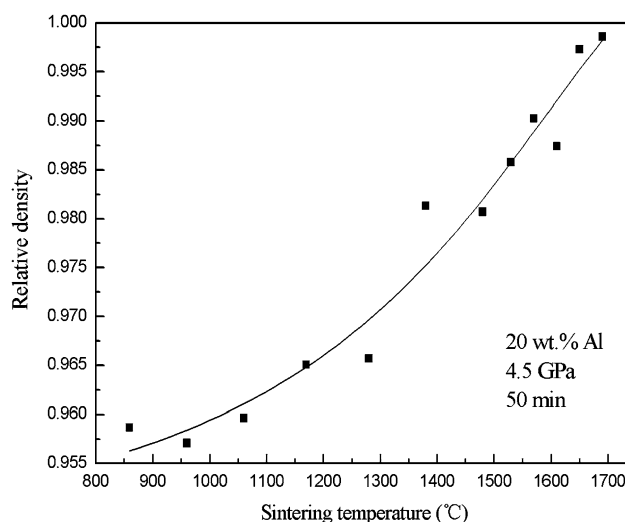


Fig. 6 Effects of sintering temperature on relative density of Al/AlN composites

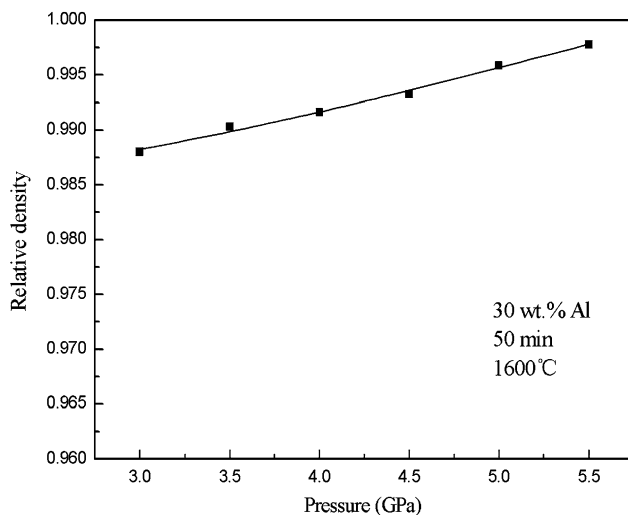


Fig. 7 Effects of pressure on relative density of Al/AlN composites

the initial stage (before 40 min). During this stage, the main mechanism is particle rearrangement, which is due to the slippage on the crystal faces and the crystal deformation because of the plastic flow and diffusion effect. The densification is obvious in this stage. In the middle and final stage (after 40 min), creep deformation plays an important role on densification, this process is a little slow. Moreover, the densification velocity has an important relationship with the diffusion of melting Al.

In pressureless sintering methods, the sintering driving force is only the surface energy. So the sintering may require more time 1–6 h [5, 6, 15]. High pressure sintering method can supply another driving force of pressure. The enhancement of driving force may result in the decrease of sintering time.

Figure 6 shows that sintering temperature has a significant effect on densification even if the sintering time is only 50 min. For the given sintering time the relative density increases obviously with the temperature increasing. The relative density value is 95.86% at 860 °C, and increases to 99.86% at 1,690 °C. Perhaps, Al/AlN composite hasn't been sintered at 860 °C, it is compaction mechanism under high pressure with a viscous liquid Al phase that make the relative density so high, and it contributes to next sintering. As can be seen from Fig. 6, the densification velocity determined by temperature is different. Relative density increases slightly slowly when the temperature is below 1,280 °C, while at high temperature (1,480–1,690 °C), relative density increases rapidly. This is because particle rearrangement and deformation as well as diffusion effect get easier at higher temperature.

Figure 7 gives the effect of pressure on relative density of Al/AlN composite. As the pressing pressure increases (3.0–5.5 GPa), relative density increases slowly and the value ranges from 98.80% at 3.0 GPa to 99.78% at

5.5 GPa. It can be calculated that the relative density has gained only 1% increase during the given pressure range. So at the given sintering time and temperature conditions, higher pressure can make the composites more compact to some extent. The mechanism of density enhancement by pressure has been studied by many people [18]. Possible densification stages were previously summarized by Macleod [19]. Four different sequential processes including: (1) particle rearrangement leading to closer packing; (2) formation of arches and vaults protecting voids and capable of supporting the applied pressure; (3) a combination of elastic, plastic, and fracture deformation mechanisms occurring simultaneously and resulting in higher density; and (4) bulk compression of the material itself.

Based on the above discussion, sintering time and temperature play the key role on the sintering at high pressure. Although at the given range (3.0–5.5 GPa) sintering pressure makes the relative density increase slightly, it facilitates the sintering and reduce the sintering conditions, for example at 5.0 GPa, the relative density can reach highly up to 99.37% for only 20 min, other methods rarely reached this level in such a short time. Therefore, the synergic effects of sintering time, temperature, and pressure contribute to the sintering process.

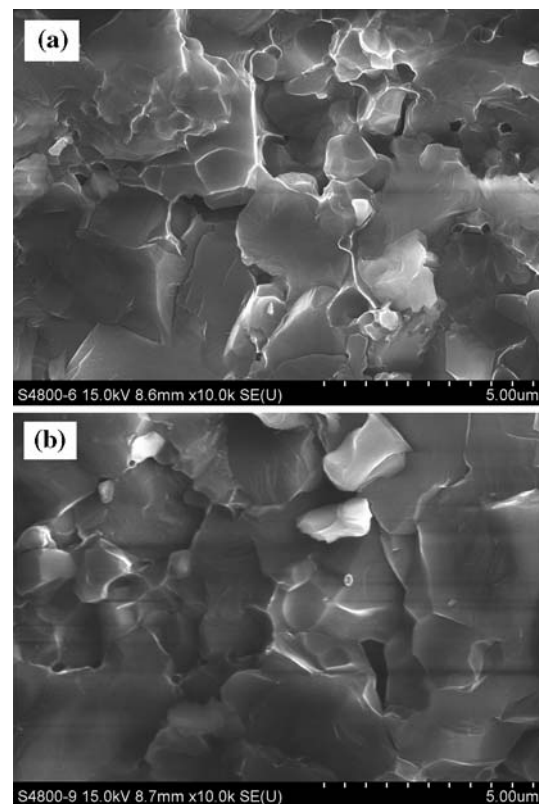


Fig. 8 SEM micrographs of fracture surfaces of Al/AlN composites (40 wt.% Al) sintered at 1,600 °C and 5.0 GPa for (a) 20 min (b) 70 min

SEM analysis

Figures 8, 9 are the SEM micrographs of fracture surfaces of Al/AlN composites sintered at the given conditions on the figures. The grey area is AlN phase and the white area is Al phase. Crystal boundaries are clear and transcrystalline fractures are easy to find. The particle size becomes more symmetrical compared with the original powder, and does not grow up basically because of the short sintering time and low temperature. Most of particles' shape becomes hexagonal, which is different from the asymmetrical shape of original powder. Most of Al phase distributes between AlN boundaries homogeneously, but a little accumulative Al phase among AlN particles can also be observed (Fig. 8). As can be seen from Fig. 8a, the structure is very dense for only 20 min, this is in agreement with the high relative density (99.37%). The grains in Fig. 9a are not sintered fully at 860 °C and some pores and isolated grains exist, so this kind of structure determines the low relative density (95.86%). Figure 9b shows a perfect microstructure of composite sintered under 4.5 GPa and 1,690 °C for 50 min. This structure of composites is very dense and homogeneous, which is difficult to obtain by conventional methods [20–22].

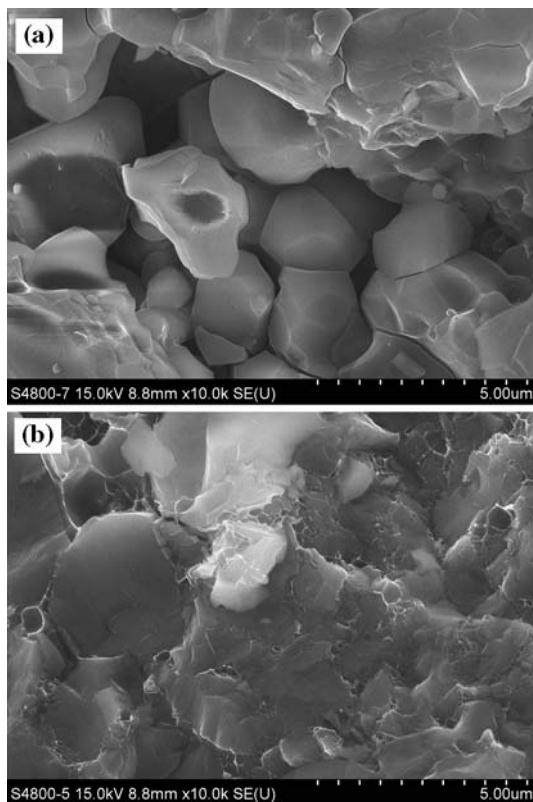


Fig. 9 SEM micrographs of fracture surfaces of Al/AlN composites (20 wt.% Al) sintered at (a) 860 °C (b) 1,690 °C and 4.5 GPa for 50 min

Conclusions

In this work, Al/AlN composites were sintered by high pressure sintering method and the effects of sintering conditions on sintering property were studied. This method is capable of producing high-density Al/AlN composites. Sintering time and temperature play an important role on sintering, and high pressure sintering method can decrease sintering time and temperature. At 5.0 GPa and 1,600 °C the relative density of composites (containing 40 wt.% Al) can reach 99.37% for only 20 min, other methods is difficult to realize this level in such a short time. Lattice parameters of the sintered specimen are found to be little smaller than those of original powder, which is the contribution of high-pressure treatment. The structure of composite is homogeneous with clear crystal boundaries. Fractures are mostly transcrystalline.

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