PROPERTIES AND MICROSTRUCTURE OF PRESSURELESS SINTERED AND MICROWAVE SINTERED SIC-ALN CERAMICS

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ABSTRACT

The microwave sintering behavior of SiC-AlN composites with the weight ratio of the two components being 3:7 at 1600°C was investigated. The pressureless sintering of SiC-AlN composites was conducted for reference in evaluating the physical and mechanical properties, as well as thermal conductivity. Y_2O_3-CaF_2 system was employed as sintering additive and argon atmosphere was applied for protection in both experiments. Microwave sintered samples with lower bulk density exhibited lower thermal conductivity but higher flexural strength. The results of microstructure observations indicated that microwave sintered composites have unique rod grains compared with the pressureless sintered particle grains. The EDS analysis of the microwave sintered SiC-AlN composite manifested that the content of SiC in rod grains was much higher than that in plate grains.

1 INTRODUCTION

Silicon carbide and aluminium nitride can form a series of solid solutions in a quite wide range of composition. However, it is difficult to fabricate dense AlN-SiC solid solutions due to the high covalence and low diffusion coefficients of AlN and SiC. Although different methods such as pressureless sintering [5], hot pressing sintering [6], spark plasma sintering [7] and combustion synthesis [8] etc. employed for the synthesis of SiC-AlN composites have been studied, the development of SiC-AlN composites have been greatly restricted by strict processing conditions of sintering time, temperature and atmosphere.

Severe sintering conditions were inevitably adopted in previous studies on the synthesis of SiC-AlN composite through pressureless sintering as the difficulty in formation of fine-grained microstructural SiC-AlN composite is widely acknowledged. As a frontline method for rapid synthesis of composites, microwave heating technique is a possible solution to the fast fabrication of high performance SiC-AlN composites. Research progresses on SiC and AlN [9-12] ceramics separately are quite encouraging using the microwave method. The result for microwave sintering of high-density (over 99.2% theoretical density), high thermal conductivity (approximately 225 W/m•K) AlN indicates that microwave sintering is a viable approach for producing AlN with superior properties when compared with conventional sintering results under similar conditions [13]. Result from a recent publication on synthesis of SiC nano powders with a graphite in a 2.45GHz microwave field in nitrogen atmosphere around 1200°C demonstrate a most efficient as well as energy-saving method for SiC powder synthesis [14]. However, microwave sintering of SiC-AlN composite has been rarely reported.

In this study, microwave sintering behavior of SiC-AlN composite doped with Y_2O_3-CaF_2 was investigated under a stable, computer-controlled microwave field. The result of conventional pressureless method was also referred as a comparison in physical, mechanical, thermal and microstructural properties. Since previous articles demonstrated the functions of sintering additives in

promoting the process of sintering and purifying the grain boundaries of the composites, Y_2O_3-CaF_2 system was applied as an addition to decrease the formation temperature of liquid phase during sintering in this study.

2 EXPERIMENTAL PROCEDURES

2.1 Chemical composition of the raw materials

Commercially available SiC powder (Aladdin Chemistry Co., Ltd, PRC, purity ≥ 99%), AlN powder (DeSheng Ceramic Materials Co., Ltd, PRC, purity ≥ 98%), Y_2O_3 powder (Aladdin Chemistry Co., Ltd, PRC, purity ≥ 99.99%), CaF_2 powder(Sinopharm Chemical Reagent Co., Ltd, PRC, purity ≥ 98.5%) were used as starting powders. A self-made organic binder was applied to improve the fluidity of the milled powders after planetary ball mills.

2.2 Preparations of green compacts and sintering

β-SiC powder and AlN powder were mixed thoroughly with 2wt% Y_2O_3-CaF_2 as sintering additive. The mixture was wet milled for 24h. The milled powder was then wet-sieved with a self-made organic binder, dried and pressed isostatically to form cubic biscuits (40mm×35mm×5mm). When employing pressureless sintering method, the specimens were sintered at 1600°C in a graphite resistance furnace (High-multi 5000, FVPHP-R-5, FRET-20, Japan) with a high purity argon atmosphere. The heating schedule was to maintain the furnace temperature at 600°C for 2 hours to remove the binder and 1600°C for 1 hour for sintering.

For samples processed with microwave sintering method, green compacts were placed in graphite crucible and covered with 50wt%-SiC-50wt%-Si_3N_4 mixed powder. Samples were heated to 1600°C in 15 minutes and maintained at this temperature for 30 minutes for sintering. Sintering was conducted in static argon atmosphere by a computer controlled heating system.

2.3 Characterization evaluation

The shrinkage of the sintered samples was measured by a vernier caliper. Bulk density and apparent porosity were determined by Archimedes' principle. The samples were cut and polished into the size of 3.0 mm×4.0 mm×35.0 mm.

Samples were processed into disks with a diameter of 12.7 mm and thickness of 3 mm for measurement of thermal conductivity using the Cowan model. Thermal diffusivity and specific heat capacity were measured by the laser flash method (LFA447, NETZSCH, Germany) at room temperature (approximately 25°C) according to the standard of GB11108-89. Thermal conductivity was then calculated using the formula:

$$\lambda = 418.68 \times \alpha \times \rho \times C_p \quad (1)$$

Where α is the thermal diffusivity, ρ is the measured bulk density of materials and C_p is the specific heat capacity.

Flexural strength was measured by the three-point flexural test with a span of 30 mm at a crosshead speed of 0.5 mm/min according to the standard of ISO 14704: 2000, MOD.

The microstructural observation was carried out by an SEM (S-4800, HITACHI corp., Japan) and elemental analysis by an energy dispersive X-ray spectrometer (EDS).

3 RESULTS AND DISCUSSION

3.1 Physical properties

	Pressureless Sintering	Microwave Sintering
Linear Shrinkage [%]	5.65	1.57
Bulk Density[g/cm^3]	2.310	1.933
Apparent Porosity [%]	27.17	37.03
Flexural strength [MPa]	93.26	106.73
Thermal conductivity[W/m•K]	17.645	5.521

Table 1: Linear shrinkage, bulk density, apparent porosity, flexural strength and thermal conductivity of the specimens.

Linear shrinkage, bulk density, apparent porosity, thermal conductivity and flexural strength of the specimens sintered by two different methods were shown in Table 1.

The pressureless sintered specimen displayed better physical properties including linear shrinkage, bulk density and apparent porosity than the microwave sintered specimen. From Table 1, it was not difficult to find that linear shrinkage of the pressureless sintered specimen was nearly 2.6 times higher than that of the microwave sintered specimen. Accordingly, the pressureless sintered specimen exhibited a 19.5% higher of bulk density than the microwave sintered specimen. The result that the pressureless sintered specimen's apparent porosity was 36.3% lower than that of the microwave sintered specimen could also prove that the pressureless sintered SiC-AlN composite had a higher level of densification than the microwave sintered specimen.

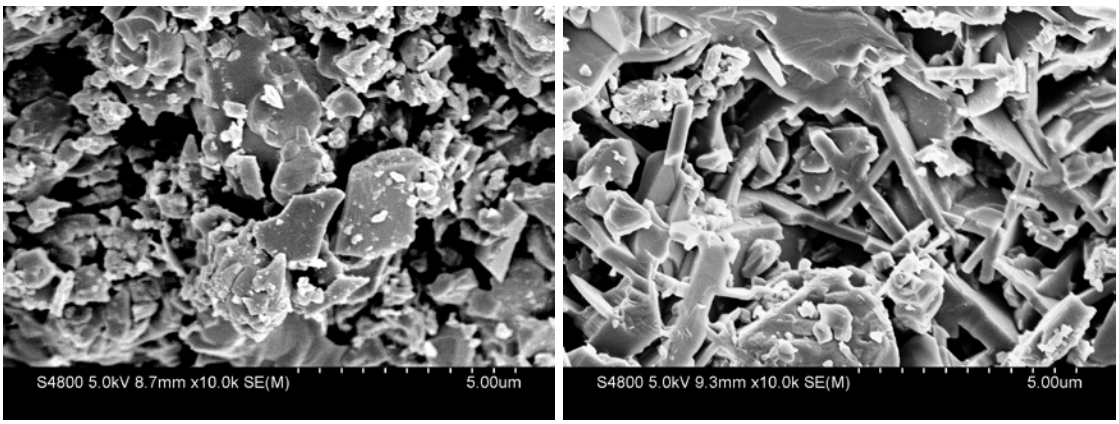
Due to its unique processing mechanism, microwave sintering is a rapid fabrication technology in dispersing microwave energy through ceramic composites. However, AlN, as the main composition in this study, was the representative of the ceramic materials which were hard to process in microwave environment because of the low dielectric loss and high sintering temperature [8]. According to the results of physical properties from microwave sintered specimen, it was not hard to deduce that the processing conditions in this study was not sufficient to form fine-grained SiC-AlN composite by the method of microwave sintering.

Thermal conductivity of the microwave sintered SiC-AlN composite was obviously lower than that of the pressureless sintered one. Oxygen in the lattice and porosity are two main factors which affect thermal conductivity of the SiC-AlN composite through the mechanism of phonon scattering [8]. For specimens sintered by two different methods, the oxygen level could be regarded as nearly equivalent when the sources such as the residual O contained in binders, oxidation of the AlN during processing, introduction from the sintering additives and contamination in experiments were taken into consideration. In view of the results of apparent porosity, it was not difficult to infer that the pressureless sintered composite with fewer pores had a higher thermal conductivity and the data of thermal conductivity testified this speculation.

Note that the microwave sintered SiC-AlN composite with lower level of densification exhibited higher flexural strength in comparison with the pressureless sintered SiC-AlN composite. This result implied that there should be some special microstructure which helped to strengthen the microwave sintered specimen.

3.2 Microstructure

The micrographs in Fig. 1 showed that the microwave sintered SiC-AlN had distinctive rod grains which connected to plate grains.



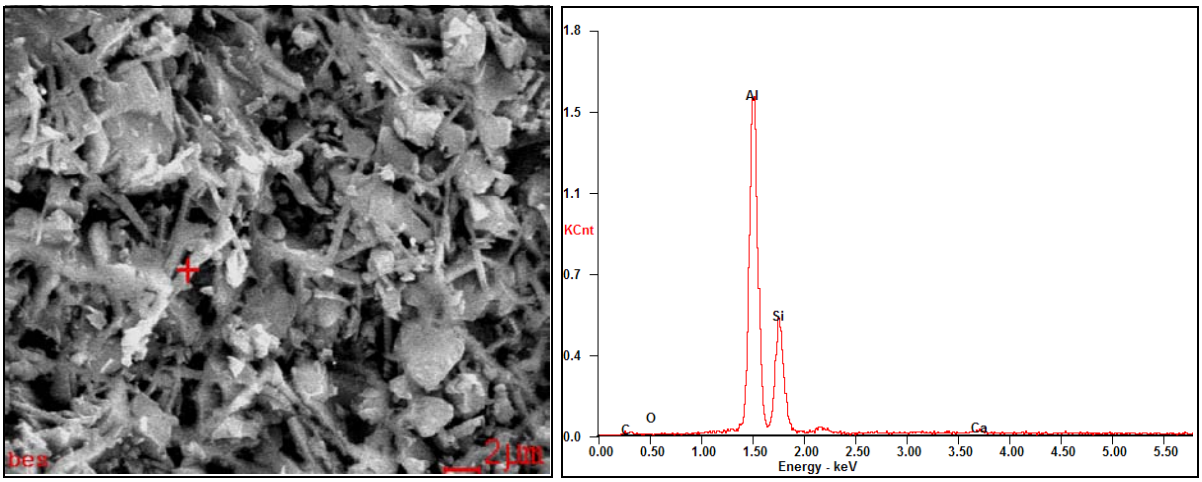
(a) (b)

Figure 1: SEM micrographs of SiC-AlN composites employing (a) pressureless method and (b) microwave method.

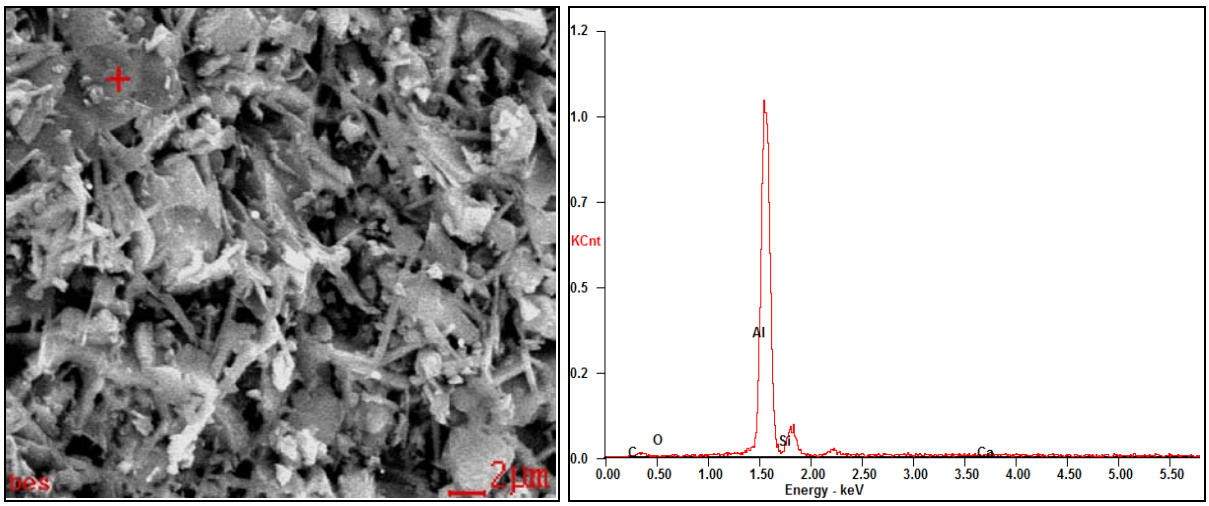
In contrast, the pressureless sintered specimen only had agglomerated plate grains and particles.

Furthermore, much fewer of isolate SiC-AlN particles dispersed on the surfaces of the grains could be found in the microwave sintered SiC-AlN composite than that of the pressureless sintered composite, indicating that the extent of reaction of microwave sintering was actually higher than pressureless sintering though the former method merely amounted to half of the latter one in sintering time.

This special microstructure could also be an explanation why specimen processed in microwave field exhibited a high-porosity result. From the micrographs, it was not difficult to find that the grains sintered in a microwave field tended to grow in anisotropy, which finally led to the formation of the rod grains. Since they were randomly distributed, the formed rod grains would intersect resulting in big holes and pores interiorly. Thus, this chaotic construction was not advantageous for the phonon's movement and caused a significant decrease in composite's thermal conductivity.



(a)



(b)

Figure 2: EDS analysis of the microwave sintered specimen at (a) rod grain and (b) plate grain.

However, the positive effect of this microstructure was the noticeable enhancement of flexural strength. A possible explanation of this result was that the rod grains disorderly grew might form some kind of bridging construction in dimensions which strengthened the materials when loaded with force exteriorly.

EDS analyses of the rod grain and the plate grain were conducted separately. Obviously, the rod grain contained much higher content of Si than that of the plate grain. When the sintering process began, SiC particles displayed higher reactive activation in response to the microwave field and started

to grow in anisotropy. However, AlN was not as sensitive to microwave as SiC and there were less AlN in rod grains than that in plate grains.

4 CONCLUSIONS

A study on the synthesis of SiC-AlN composite was conducted. The composite of SiC-30wt. %-AlN-70%wt. % with 2wt. % Y_2O_3-CaF_2 as sintering additive sintered in Ar atmosphere under microwave field was synthesized and characterized. The microwave sintered specimen had a linear shrinkage of 1.57 %, bulk density of 1.933 g/cm^3, apparent porosity of 37.03 %, which was regarded as a sign that the microwave sintered SiC-AlN composite showed a lower level of densification than the pressureless sintered SiC-AlN composite. Thermal conductivity of the microwave sintered SiC-AlN composite was 5.521 W/m•K which was found closely related to the result of apparent porosity.

Due to its special rod-grains microstructure, the microwave processed SiC-AlN composite displayed a higher flexural strength of 106.73 MPa compared with the pressureless sintered specimen, indicating that distinctive microstructure formed by the microwave method played an important role in strengthening the SiC-AlN composite. EDS analyses of rod grain and plate grain showed that SiC took a leading role in forming rod grains.

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