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Preparation and properties of SiO_2 matrix composites doped with AlN particles

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SiO_2 matrix composites doped with AlN particles were prepared by hot-pressing process. Mechanical properties of SiO_2 matrix composites can be greatly improved by doping with AlN particles. Flexural strength and fracture toughness of 30 vol%AlN-SiO_2 composite sintered at 1400 °C reached 200 MPa and 2.96 MPa·$m^{1/2}$. XRD analysis indicated that, up to 1400°C, no chemical reaction occurred between SiO_2 matrix and AlN particles suggesting an excellent chemical compatibility of SiO_2 matrix with AlN particles. The influences of hot-pressing temperature and the content of AlN particles on dielectric properties of SiO_2-AlN composites were studied. The temperature and frequency dependency of dielectric properties of SiO_2-AlN composites were also studied. Residual flexural strength of SiO_2-AlN composites decreased with increasing temperature difference. The critical temperature difference was estimated about 600°C.

1. Introduction

The excellent dielectric properties of SiO_2 make it a superior candidate for use as electromagnetic window materials [1]. However, low mechanical properties limit its extensive application. AlN exhibits excellent properties such as low dielectric constant and dissipation factor and high flexural strength and elastic modulus [2]. According to the multiphase ceramic viewpoints flexural strength and fracture toughness of the matrix can be enhanced by doping with the second-phase particle, fibre or whisker [3, 4]. Therefore, it is reasonable to believe that, when doping with AlN particles, flexural strength and fracture toughness of SiO_2 matrix composites can be improved to a certain extent. In this paper SiO_2 matrix composites doped with AlN particles were prepared by hot-pressing process. Properties such as mechanical, dielectric and thermal properties of SiO_2-AlN composites were investigated.

2. Experimental procedure

2.1. Sample preparation

SiO_2-AlN composites with various content of AlN particles of 10, 20 and 30 vol% were prepared using amorphous SiO_2 powders (99.98% pure) and AlN particles (synthesised from SHS method, $N > 33.06$ wt%, $O < 0.36$ wt%) as starting materials. The batches with various content of AlN particles were firstly ball-mixed for 24 h using ethanol as media. The resultant mixtures were dried, ground and then sifted. Finally powder compacts were hot-pressed to fabricate SiO_2-AlN composites in graphite dies in the Ar atmosphere at 1250°C, 1300°C, 1350°C and 1400°C with a pressure of 20 MPa and holding time of 30 min.

2.2. Characterization

The bulk density of SiO_2-AlN composites was determined by Archimedes Method. The crystalline phase of the composites was identified by X-ray diffractometry (Model Rigaku RAX-10C). Mechanical properties were examined by three-point bend test using an Instron 1195 Universal Test Machine. The sample sizes were $2.5 \times 5 \times 30$ mm for flexural strength and $5 \times 2.5 \times 30$ mm for fracture toughness. The support span was 20 mm. The loading speed was 0.25 mm·min^{-1} for flexural strength and 0.05 mm·min^{-1} for fracture toughness. The fracture surfaces of the composites were observed by SEM analysis (Model Shimadzu EPMA-8705 QHII). The microstructure of the composites was examined by TEM analysis (Model JEM-200CXJ). Dielectric properties of the composites were measured in the frequency range 10 KHz to 3 MHz by bridge method using an Ando TR-10C Dielectric Loss Measuring Set. The sample size was $\phi 22.5 \times 1.5$ mm. Thermal expansion coefficient was measured using a Netzsch 402ES-3 Push Rod Dilatometer with heating rate of 5°C·min^{-1}. The sample size was $4 \times 4 \times 30$ mm. Thermal conductivity was examined from thermal diffusivity measured by laser flash technique and specific heat capacity and bulk density. The sample size was $16 \times 4 \times 0.3$ mm. Thermal shock tests were conducted by measuring residual flexural strength after quenching samples from 600°C, 800°C and 1000°C into cold water (20°C).

3. Results and discussion

3.1. Sintering and phase composition

Fig. 1 showed relative density of SiO_2-AlN composites with various content of AlN particles as a function

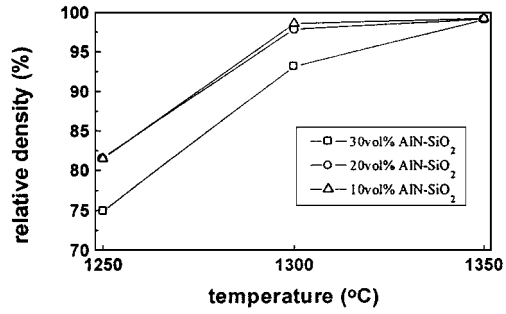


Figure 1 Relative density of SiO_2-AlN composites as a function of hot-pressing temperature.

of hot-pressing temperature. It can be found that relative density of the composites increased with increasing hot-pressing temperature; while in the same hot-pressing temperature relative density decreased with increasing the content of AlN particles, indicating that doping with AlN particles impeded the densification process of the composites. When sintered at 1350°C, relative densities of SiO_2-AlN composites with various content of AlN particles were above 99%, which confirmed that the fully dense composites can be produced in the SiO_2-AlN system.

Fig. 2 showed XRD patterns of SiO_2-AlN composites with various content of AlN particles. It can be found that, for 10 vol%AlN-SiO_2 composite and 20 vol%AlN-SiO_2 composite, no cristobalite was formed when sintered at 1300°C; while sintered at 1350°C, there was cristobalite precipitated. But the intensity of diffraction peak of cristobalite in the 20 vol%AlN-SiO_2 composite was weaker than that in the 10 vol%AlN-SiO_2 composite. For 30 vol%AlN-SiO_2 composite the precipitation of cristobalite cannot be detected when sintered at 1350°C. However, when sintered at 1400°C, the diffraction peak of cristobalite became very sharp. The above-obtained XRD results indicated that the precipitation of cristobalite can be retarded to higher hot-pressing temperature with increasing the content of AlN particles, that is, in the same hot-pressing temperature the precipitation of cristobalite can be refrained by doping with AlN particles. In addition, it can also be found from Fig. 2 that no other diffraction peak can be detected except diffraction peak of cristobalite and AlN for all the composites, suggesting that no chemical reaction occurred between SiO_2 matrix and AlN particles. It can be concluded that SiO_2 matrix and AlN particles can retain their distinctive properties with good chemical compatibility up to 1400°C.

3.2. Mechanical properties and microstructure

Fig. 3 and Fig. 4 showed flexural strength and fracture toughness of SiO_2-AlN composites with various content of AlN particles as a function of hot-pressing

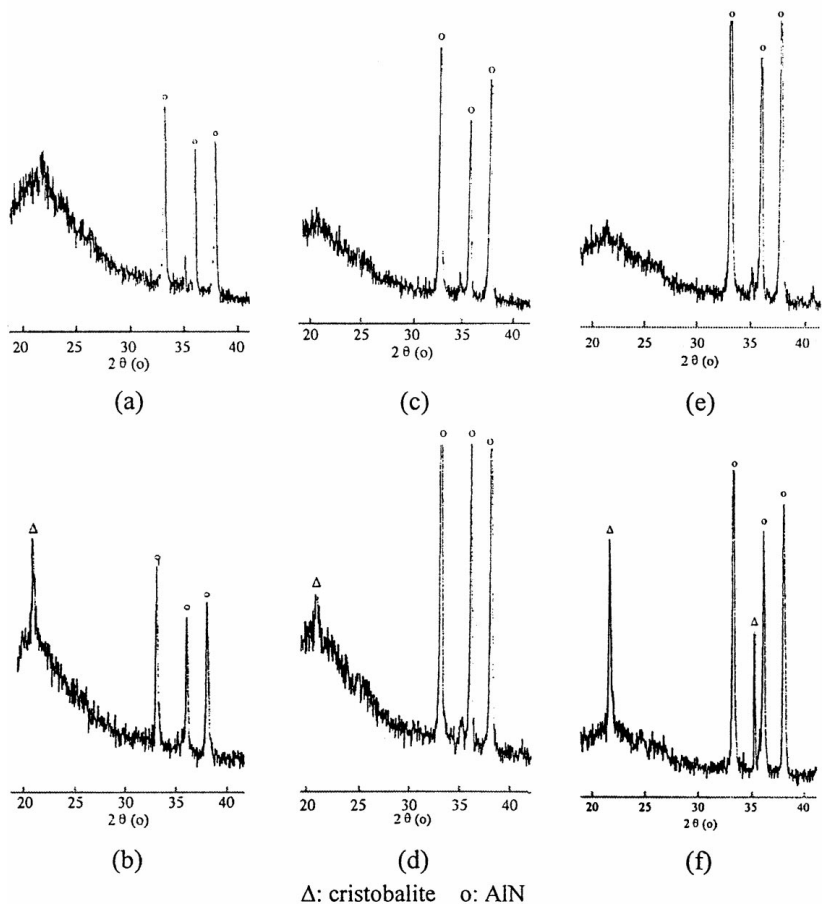


Figure 2 XRD patterns of SiO_2-AlN composites. (a) 10 vol%AlN-SiO_2 sintered at 1300°C; (b) 10 vol%AlN-SiO_2 sintered at 1350°C; (c) 20 vol%AlN-SiO_2 sintered at 1300°C; (d) 20 vol%AlN-SiO_2 sintered at 1350°C; (e) 30 vol%AlN-SiO_2 sintered at 1350°C; (f) 30 vol%AlN-SiO_2 sintered at 1400°C.

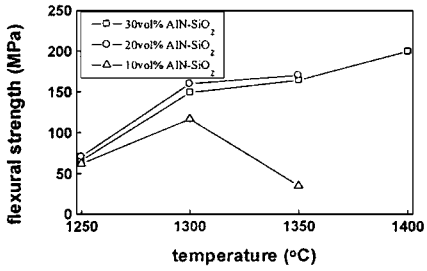


Figure 3 Flexural strength of SiO_2-AlN composites as a function of hot-pressing temperature.

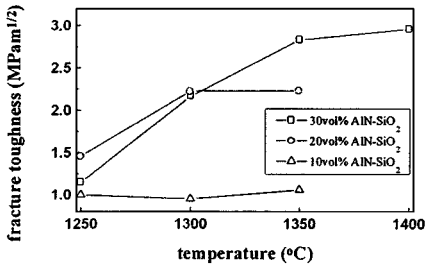


Figure 4 Fracture toughness of SiO_2-AlN composites as a function of hot-pressing temperature.

temperature. For 10 vol%AlN-SiO_2 composite flexural strength reached the maximum value 117 MPa when sintered at 1300°C, then decreased abruptly when sintered at 1350°C; while fracture toughness remained around 1 MPa·$m^{1/2}$. The abrupt decrease of flexural strength and approximate invariance of fracture toughness were perhaps due to the fact that excessive cristobalite was precipitated resulting in the formation of microcrack in the body of the composite. With increasing the content of AlN particles, because of the refrained precipitation of cristobalite (thus the induced microcrack in the composites was reduced) and doping with AlN particles with high elastic modulus, flexural strength and fracture toughness of the composites increased with increasing hot-pressing temperature. For 30 vol%AlN-SiO_2 composite sintered at 1400°C flexural strength and fracture toughness reached the best results 200 MPa and 2.96 MPa·$m^{1/2}$, increasing by 3.16 and 1.96 times greater than those of SiO_2 matrix [5]. This meant that flexural strength and fracture toughness of SiO_2-AlN composites can be significantly improved by doping with AlN particles. Therefore, it can be concluded that doping with AlN particles reinforced SiO_2 matrix composites.

Fig. 5 showed SEM micrograph of fracture surfaces of SiO_2-AlN composites with various content of AlN particles. Fig. 5a showed that there existed microcrack in the body of 10 vol%AlN-SiO_2 composite sintered at 1350°C, which caused the deterioration of mechanical properties of the composite. Fig. 5b and Fig. 5c showed that the fracture surfaces of the composites became rougher with increasing the content of AlN particles, allowing fracture surfaces to take on the zigzag form. Apparently, such a microstructure offered the major contribution to the unique mechanical properties of SiO_2-AlN composites.

Fig. 6 showed TEM micrograph of SiO_2-AlN composites. According to the toughening principle, when the composites are cooled from hot-pressing temperature to room temperature, the difference between thermal expansion coefficient of the matrix and the reinforcer will cause the formation of residual stress field in the body of the composites, and thus the microcrack will deflect, diverge and even pin when propagating around residual stress field. The difference between thermal expansion coefficient of SiO_2 matrix ($\alpha = 0.5 \times 10^{-6}\,K^{-1}$) and AlN particles ($\alpha = 4.5 \times 10^{-6}\,K^{-1}$) was great so that, when propagating, microcrack would deflect, diverge and even pin, as showed in Fig. 6. Microcrack deflection, microcrack divergence and microcrack pinning increased the hindering force and consumed the propagating energy and thus reinforced the composites.

3.3. Dielectric properties

Table I showed the data of dielectric properties of 20 vol%AlN-SiO_2 composites as a function of hot-pressing temperature. In the frequency range 100 KHz to 3 MHz dielectric constant increased and dissipation factor decreased with hot-pressing temperature, which was in accordance with the densification behaviour of SiO_2-AlN composites due to the fact that the presence of porosity would cause decrease of dielectric constant and increase of dissipation factor.

Fig. 7 showed dielectric constant of 20 vol%AlN-SiO_2 composites as a function of relative density in the frequency 100 KHz. These data were plotted using the formula given by J. P. Walton Jr. [6] to relate dielectric constant for porous and fully dense materials as:

$$\varepsilon = \varepsilon_0^{(1-p)} \tag{1}$$

where ε_0 is dielectric constant of fully dense material and $(1 - p)$ is relative density. From these data a dielectric constant smaller than that derived from mixture rule [7] for fully dense 20 vol%AlN-SiO_2 composite would be predicted. The reason was perhaps due to the presence of porosity in the composites.

In order to make meaningful understand on the influence of doping with AlN particles on dielectric properties of the composites, SiO_2-AlN composites sintered at 1250°C were selected. Table II showed the data of dielectric properties of SiO_2-AlN composites sintered at 1250°C as a function of the content of AlN particles. It can be found that dielectric constant and dissipation factor increase with increasing the content of AlN particles which corresponded to the fact that dielectric constant and dissipation factor of AlN particles are higher than those of SiO_2 matrix.

Fig. 8 showed the temperature dependency of dissipation factor of 20 vol%AlN-SiO_2 composites in

TABLE I Dielectric properties of 20 vol%AlN-SiO_2 composites as a function of hot-pressing temperature

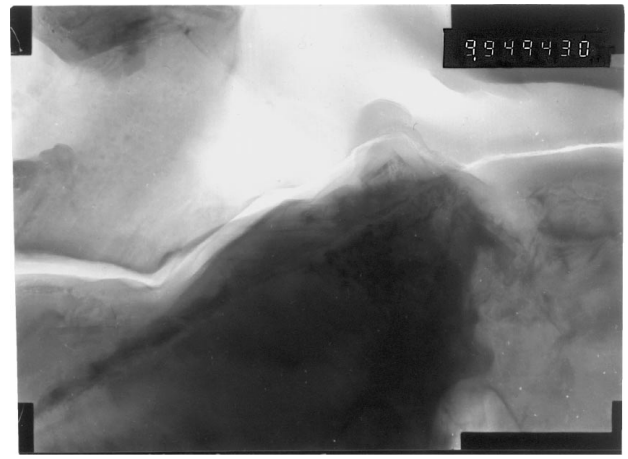
hot-pressing temperature	1250°C		1300°C		1350°C	
	ε	tgδ	ε	tgδ	ε	tgδ
100 KHz	4.1	5.0×10^{-1}	5.6	9.0×10^{-2}	5.9	1.3×10^{-3}
1 MHz	5.2	1.1×10^{-1}	5.3	3.1×10^{-2}	5.8	5.0×10^{-4}
3 MHz	5.2	3.4×10^{-2}	5.4	7.0×10^{-3}	5.7	3.0×10^{-4}

(a)

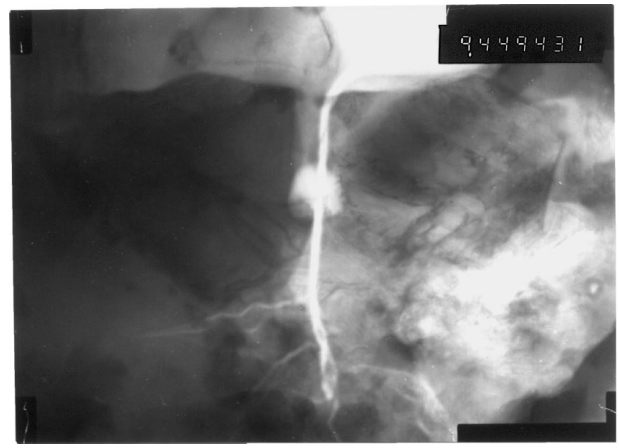
(b)

(c)

Figure 5 SEM micrograph of fracture surfaces of SiO_2-AlN composites. (a) 10 vol%AlN-SiO_2 sintered at 1350°C; (b) 20 vol%AlN-SiO_2 sintered at 1350°C; (c) 30 vol%AlN-SiO_2 sintered at 1400°C.



(a)



(b)

(c)

Figure 6 TEM micrograph of SiO_2-AlN composites showing (a) microcrack deflection and (b) microcrack divergence and (c) microcrack pinning.

the frequency 1 MHz. As shown in Fig. 8, the temperature had a critical effect on dissipation factor for 20 vol%AlN-SiO_2 composites sintered at 1250°C and 1300°C. However, for the composite sintered at 1350°C, it seemed that dissipation factor was independent of temperature over the whole range from RT to 200°C. The similar temperature dependency of dissipation factor has also been plotted for 10 vol%AlN-SiO_2 composites and 30 vol%AlN-SiO_2 composites. This meant that excellent temperature stability of dielectric properties can be achieved for SiO_2-AlN

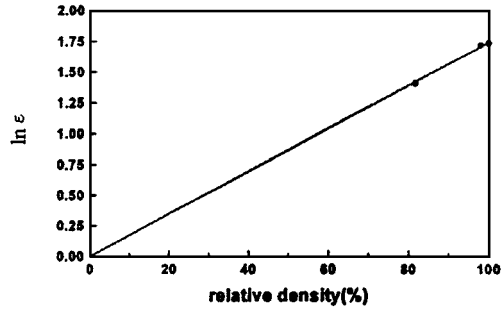


Figure 7 Dielectric constant of 20 vol%AlN-SiO_2 composites as a function of relative density.

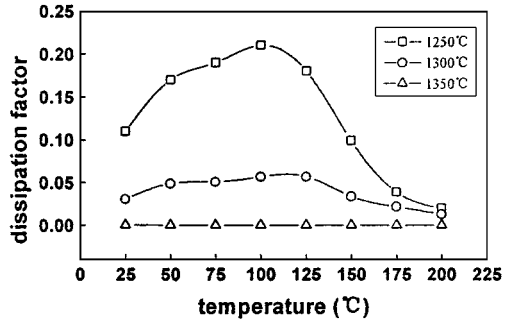


Figure 8 Temperature dependency of dielectric properties of 20 vol%AlN-SiO_2 composites.

TABLE II Dielectric properties of SiO_2-AlN composites as a function of the content of AlN particles

the content of AlN particles	10		20		30	
	ε	tgδ	ε	tgδ	ε	tgδ
1 MHz	4.1	9.0×10^{-4}	5.2	1.1×10^{-1}	6.3	2.0×10^{-1}
3 MHz	4.1	5.0×10^{-4}	5.2	3.4×10^{-2}	5.9	5.0×10^{-2}

composites with various content of AlN particles sintered at 1350°C, which was in good agreement with dielectric behaviour of SiO_2 matrix [6].

In a wide range of dielectric materials, it is generally found that the frequency dependency of dielectric properties follows the universal principle suggested by A. K. Jonscher [8, 9]:

$$\varepsilon' \propto \omega^{n-1} \tag{2}$$

where $\varepsilon' = \varepsilon \cdot \text{tg}\delta$, $0 < n < 1$. With the present composites the experimental evidences indicated that dielectric loss ε' was proportional to ω^{n-1} in the frequency range 10 KHz to 3 MHz. Fig. 9 showed the typical frequency dependency of dielectric loss of 20 vol%SiO_2-AlN composite sintered at 1350°C indicating that the data fitted well with the universal principle. Table III showed the value of n for SiO_2-AlN composites with various content of AlN particles sintered at 1300°C and 1350°C. It seemed that the value of n increased progressively with increasing the content of AlN particles and hot-pressing temperature for all the composites except for 30 vol%AlN-SiO_2 composite sintered at 1300°C.

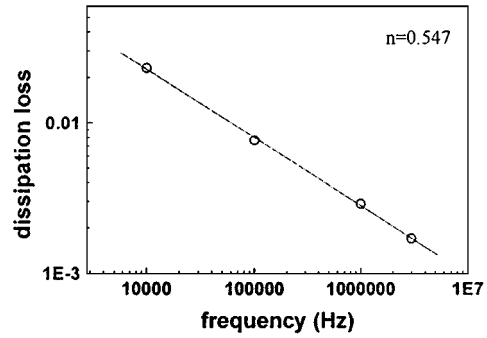


Figure 9 Frequency dependency of dielectric loss of 20 vol%AlN-SiO_2 composite sintered at 1350°C.

TABLE III Fitness check of experimental data and universal principle

n	10	20	30
1300°C	0.331	0.442	0.217
1350°C	0.401	0.547	0.572

TABLE IV Thermal conductivity of SiO_2-AlN composites as a function of hot-pressing temperature

thermal conductivity ($W\cdot m^{-1}\cdot K^{-1}$)	1250°C	1300°C	1350°C	calculated value
20 vol%AlN-SiO_2	1.166	2.525	2.926	3.412
30 vol%AlN-SiO_2	1.413	2.616	3.156	4.457

3.4. Thermal properties

Fig. 10 showed thermal expansion coefficient of SiO_2-AN composites with various content of AlN particles sintered at 1350°C as a function of temperature. It can be found that thermal expansion coefficient increased with increasing temperature, while in the same temperature thermal expansion coefficient increased with increasing the content of AlN particles at high temperature. However, below 400°C, the abnormal changes of thermal expansion coefficient with the content of AlN particles were measured. This reflected the presence of microcrack induced by the difference between thermal expansion coefficient of SiO_2 matrix and AlN particles due to the fact the microcrack tended to close on heating. In the temperature range RT-1200 °C the average thermal expansion coefficient

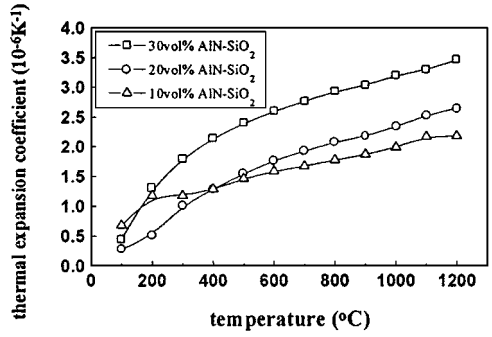


Figure 10 Thermal expansion coefficient of SiO_2-AlN composites as a function of temperature.

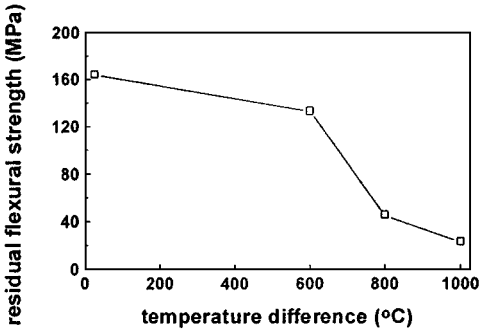


Figure 11 Residual flexural strength of 30 vol%AlN-SiO_2 composite after thermal shock as a function of temperature difference.

Figure 12 SEM micrograph of fracture surface of 30 vol%AlN-SiO_2 composite after thermal shock.

was $3.46 \times 10^{-6}\,K^{-1}$ for 30 vol%AlN-SiO_2 composite, $2.65 \times 10^{-6}\,K^{-1}$ for 20 vol%AlN-SiO_2 composite and $2.18 \times 10^{-6}\,K^{-1}$ for 10 vol%AlN-SiO_2 composite indicating the large increase of thermal expansion coefficient with doping with AlN particles. Obviously this would take effect on thermal shock resistance of the composites.

Table IV showed the data of thermal conductivity of SiO_2-AlN composites with various content of AlN particles as a function of hot-pressing temperature. It can be found that thermal conductivity increased with hot-pressing temperature and the content of AlN particles.

Since AlN particles were dispersed in a continuous SiO_2 matrix, thermal conductivity of the composites was closer to that of SiO_2 matrix ($\lambda = 1.95\ w{\cdot}m^{-1}{\cdot}K^{-1}$) than that of AlN particles ($\lambda = 320\ w{\cdot}m^{-1}{\cdot}K^{-1}$).

The presence of microcrack resulted in the lower thermal conductivity compared with those calculated from the formula concerning conductivity of multi-phase ceramics [6].

The changes in residual flexural strength of 30 vol%AlN-SiO_2 composite sintered at 1350°C after thermal shock as a function of temperature difference were presented in Fig. 11. Because of the presence of thermal stress developed when subjected to a rapid change in temperature residual flexural strength tended to decrease with increasing temperature difference. When temperature difference was below 600°C, residual flexural strength decreased slowly no more than 20%. However, when temperature difference was equal to 800°C, residual flexural strength decreased abruptly by 70% showing the feature of kinetic microcrack propagation. The critical temperature difference was estimated about 600°C. Fig. 12 showed SEM micrograph of fracture surface of 30 vol%AlN-SiO_2 composite after thermal shock. The porous microstructure has been observed accompanying with some voids which reflected thermal spalling of AlN particles from SiO_2 matrix due to poor bonding between SiO_2 matrix and AlN particles after thermal shock. For a material with excellent thermal shock resistance the favourable characteristics, such as low thermal expansion coefficient and high flexural strength, were required. However, for the present composites, doping with AlN particles resulted in the increase of both thermal expansion coefficient and flexural strength. Thus, no improvement in thermal shock resistance was obtained.

4. Conclusions

Flexural strength and fracture toughness of SiO_2-AlN composites can be significantly enhanced by doping with AlN particles. Microcrack deflection, microcrack divergence and microcrack pinning were the main toughening mechanism. With increasing hot-pressing temperature dielectric constant increased and dissipation factor decreased; while in the same hot-pressing temperature dielectric constant and dissipation factor increased with increasing the content of AlN particles. The temperature dependency of dielectric properties showed that dissipation factor of SiO_2-AlN composites sintered at 1350°C was independent of temperature. The frequency dependency showed that the variation of dielectric loss with frequency followed the universal principle. The critical temperature difference of SiO_2-AlN composites was estimated about 600°C. The doping with AlN particles didn't resulted in the perceptible improvement in thermal shock resistance.

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