

THERMAL PROPERTIES OF ZIRCONIA TOUGHENED ALUMINA CERAMICS WITH BORON NITRIDE NANOTUBES

Kim H.T.,* Kim C.H., and Go E.B.

*Author for correspondence

Nano Materials Convergence Centre

Korea Institute of Ceramic Engineering and Technology

Jinju, 52851,

Republic of Korea,

E-mail: hytek@kicet.re.kr

ABSTRACT

The demand for high thermal conductivity substrates with electrically insulating materials are increasing with the emerging markets in power electronics and mobile telecommunication device packages. Effective heat transfer in those packages is important to provide high performance and reliability of the product. This paper presents the microstructure and thermal properties of zirconia toughened alumina ceramics with the addition of small amount of boron nitride nanotubes, BNNTs. The effect of the addition of BNNTs on the sintering behavior, the microstructure and the thermal conductivity of the zirconia toughened alumina, YZTA, nanocomposite ceramics are investigated. The thermal conductivity of YZTA ceramics decreased dramatically with the amount of zirconia contents due to relatively low thermal conductivity of zirconia ceramic. However, the addition of BNNTs less 0.5wt% to the YZTA ceramics slightly increased the thermal conductivity but decreased the coefficient of thermal expansion about 20%. The structure properties relation on this composite system is discussed.

INTRODUCTION

Recently, thermal conductivity has become an important parameter when lowering the thermal resistance of integrated electronics and power device packages for efficient heat dissipation and reliability [1, 2]. The demand for ceramic substrates with high mechanical strength and high thermal conductivity is growing due to their use in thinner profile and high-power device packaging substrates. Examples are direct bonded copper or aluminium (DBC or DBA) or direct plated copper (DPC) substrates for insulated gate bipolar transistors (IGBT) [1], thin and robust ceramic package for image sensor module (ISM) that is used in mobile smart phones, ceramic packages for miniaturized chip type supercapacitors, and high-power LED packages [2].

Alumina is a typical ceramic package substrate material [3] due to its excellent physical properties such as high thermal, corrosion and wear resistance, as well as good electrical insulation. To improve its mechanical strength further, zirconia (ZrO_2) or yttria-stabilized zirconia (YSZ) has been added to alumina as a toughening agent [4], so called zirconia-toughened alumina, ZTA ceramics. There is abundance of mechanical

properties information on ZTA ceramics since they are mostly used in the structural ceramics and electronic packaging industry. The thermal conductivities of selected compositions such as 15 vol% zirconia containing alumina (15ZTA) or 25 vol% zirconia containing alumina (25ZTA) are known by the manufacturer's technical data sheet, but it is hardly found the comprehensive information on the thermal conductivity of ZTA ceramic composite system.

Boron nitride nanotubes (BNNTs) are known as a wide-bandgap material (> 5 eV), and they have a high mechanical strength of about 1.18 TPa (similar to carbon nanotubes at ~ 1.33 TPa), high oxidation resistance over 800°C , high thermal and chemical stability, and a thermal neutron absorption capability. Thus, BNNTs can be used in many applications, such as a toughening agent for engineering ceramics or as a high heat transfer material due to its electrical insulation and high thermal conductivity. Also, it can be applied in biomedical applications or as a γ -ray shielding material for aerospace architectures [5].

NOMENCLATURE

c [-] Proportion of component

Special characters

α [-] Structural constant

κ [W/mK] Thermal conductivity

Subscripts

m Matrix phase

f Filler phase

The addition of small amounts of BNNTs (0.5 wt%) to alumina or Si_3N_4 engineering ceramics greatly enhances their high-temperature superplastic deformation by decreasing the stress under deformation conditions [6]. The thermal shock resistance behaviour of γ -alumina composites containing 2.0 wt% BNNTs was investigated and no significant improvement in thermal shock resistance was found, although the flexural strength was higher than that of the material without BNNTs. The flexural strength and thermal conductivity of an alumina composite containing BNNTs was 532 MPa and 6.9 W/m·K,

respectively, while that of an alumina monolith was 318 MPa and 6.3W/m·K, respectively [7]. This improvement in flexural strength was explained as a result of the grain growth inhibition of γ -alumina as well as the bridging of BNNTs at the grain boundaries and the physical bonding between BNNTs and the alumina matrix [8]. The flexural strength of zirconia ceramics strengthened by BNNTs and sintered by the hot-press method was seen to increase due to grain boundary strengthening and a boost to the zirconia phase transition by the BNNTs [9]. Strengthening of 3 mol% yttria-stabilized tetragonal zirconia (3Y-TZP) ceramics via a BNNT addition was also reported with the use of the spark plasma sintering (SPS) process, and the fracture toughness was found to increase about 100% by the addition of 2.5 wt% multi-walled BNNTs. The strengthening mechanism was explained by the trans-granular fracture mode due to stronger grain boundaries with BNNTs [10].

There were so many studies on the mechanical properties change or improvement via toughening of alumina by zirconia or YSZ and via the phase transformation of zirconia by chemical doping of yttria etc. [3, 4, 8-10]. However, there are not many studies on the thermal properties of alumina or ZTA compared to the mechanical studies. Recent studies on thermal diffusivity of ZTA composites with YSZ amount reported only a thermal diffusivity data of ZTA containing up to 10 vol% of 5YSZ [11]. Their results highlighted that the decrease in both grain size and porosity content reduces the thermal diffusivity. Moreover, the thermal conductivities of yttria-stabilized zirconia (YZTA) composites with BNNT remain unknown. This paper presents the effect of BNNT addition on the structure and thermal properties of YZTA base ceramics. These ceramics are made via simple pressure-less sintering to broaden the range of applications.

EXPERIMENTAL PROCEDURE

Alpha-alumina (α -Al₂O₃) powders (Nanostructured & Amorphous Materials Inc., Houston, TX) with 150 nm average particle size (D_{50}) and 99.97% purity were used as a matrix phase. Two samples, including pure alumina and an alumina composite containing 25 vol% of 3 mol% yttria-stabilized zirconia (3YSZ), herein referred to as YZTA, were fabricated as a reference. The reference sample was fabricated because the sintering behaviour and physical properties can be varied upon various experimental conditions such as the raw materials purity, particle size and distribution, morphology etc., even though there are plenty of reference data for ZTA and YZTA ceramics. YZTA powder containing 3YSZ nanopowder (Nanostructured & Amorphous Materials Inc., Houston, TX) with 40 nm particle size and 99.9% purity were mixed with BNNT powders in the range of 0.1 wt% - 0.5 wt% (herein referred to as YZTA-BNNT). BNNTs (product code: BNNT-R, TEKNA Advanced Materials Inc., Sherbrooke, Quebec) with a nanotube diameter of 5 nm, a surface area > 100 m²/g, and BNNT phase content > 60% with elemental B < 25% were used as a secondary toughening agent added to the ZTA ceramics.

As-received powders containing α -alumina, 3YSZ powder, and BNNTs in a given formulation were weighed and mixed in a Teflon jar for 6 h at 130 rpm, using zirconia ball media and an

ethanol solvent. The mixed slurry was dried in an oven at 85°C for 24 h, and the dried powder cake was hand crushed in an agate mortar and sieved with a 70 mesh. Then, the fine powder was granulated with 10 wt% PVA solution (in DI water). The mixed powder granules were used to form two types of discs with $\phi \times t = 15.5\text{mm} \times 2\text{mm}$ for the thermal conductivity measurement, using a uniaxial press under 100 MPa. The pressed green ceramic compacts were sintered at 1,600°C ~1,700°C for 4 h in a 3% H₂-N₂ atmosphere. The heating and cooling rate was 10°C/min.

The densities of the sintered pure alumina, YZTA, and YZTA-BNNT composite samples were measured by the Archimedes method (ASTM 373-88). The thermal diffusivities of the samples were measured by the laser flash method (model LFA-427, Netzsch, Selb, Germany), and the thermal conductivities were calculated from the following equation:

$$\begin{aligned} \text{Thermal conductivity } (\kappa = W/m \cdot K) \\ = \text{Thermal diffusivity } (mm^2/s) \times \text{density } (g/cm^3) \\ \times \text{heat capacity } (J/gK) \end{aligned} \quad (1)$$

The microstructures of the alumina composites were observed using transmission electron microscopy (TEM: model JEM-3000F, ZEOL, Tokyo, Japan) and field emission scanning electron microscopy (FE-SEM: model ZSM-7610F, ZEOL, Tokyo, Japan), with energy dispersive spectroscopy (EDS) and elemental mapping images to analyze the chemical elements in the microstructure.

RESULTS AND DISCUSSIONS

In this work, pure alumina and 25YZTA samples were fabricated as a reference for the YZTA-BNNTs composites. The mechanical and thermal properties of the samples are greatly influenced by the samples' purity, starting powder particle size and distribution, surface area, and sintering conditions. The sintered density, flexural strength, and thermal conductivity of the two reference samples are summarized in Table I. Pure alumina samples with 99.97% purity and 99.0-99.5% relative densities when sintered at 1,600-1,700°C for 4h exhibited the flexural strength less than 305MPa at this pressure-less sintering condition. However, the room temperature thermal conductivities were 32.8-35.7 W/mK which is quite similar values to the previous work, 33 W/mK [3].

Table I. Flexural strength and thermal conductivity of alumina and 25YZTA ceramics as reference data

Composition	Density [g/cc] (% relative)	Flexural strength [MPa]	Thermal conductivity [W/mK]
Alumina (99.97% Al ₂ O ₃)	3.90-3.93 (99.0-99.5)	203-305	32.8-35.7
25YZTA (25 vol% 3YSZ)	4.22-4.33 (93.9-96.7)	323-450	21.0-22.4

The flexural strength of pure alumina that sintered at 1,650°C was 305 MPa, and it was increased up to 450MPa due

to grain growth inhibition of alumina and toughening, when 25 vol% of 3YSZ was added. However, the thermal conductivity was decreased from 35.7 to 22.4 W/m·K with the addition of 25 vol% 3YSZ that has a low thermal conductivity of 2.0-2.5 W/mK

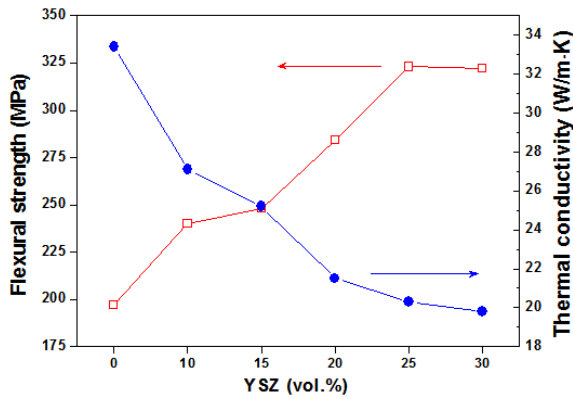


Figure 1 Thermal conductivities and flexural strengths of ZTA ceramic composites with the amount of YSZ content.

Fig. 1 shows the flexural strength and thermal conductivity changes upon the variation of YSZ amount. The flexural strength was increased from 200MPa to 325MPa when 25 vol% of YSZ was included but no further enhancement was observed over 25 vol%. Moreover, the thermal conductivities dropped severely with the addition of YSZ. Therefore, the starting ZTA composition for this experiment was determined to 25 vol% YSZ containing alumina, i.e. 25YZTA. The tentative application is targeted on robust alumina base thin substrate with high thermal conductivity for power device packaging. As we can see in the figure, the relation between the flexural strength and the thermal conductivity is a trade-off upon the amount of zirconia or YSZ. Therefore, the selection of YZTA composition may depends on the target application.

The theoretical and sintered bulk densities of the 25YZTA-BNNT samples are plotted in Fig. 2 versus the amount of BNNT and for various sintering temperatures. The theoretical density of ZTA ceramics with 25 vol% YSZ is 4.49g/cc, and this decreased gradually with increased addition of BNNTs. The maximum sintered density was obtained for the 25YZTA sample with 0.3 wt% BNNTs that was sintered at 1,700°C for 4 h. The density decreased for the samples with further addition of BNNTs.

The 25YZTA sample sintered at 1,700°C with BNNT over 0.3 wt% addition resulted in the weak mechanical strength, similar to the density data shown in Fig. 2. It is expected that the high content of impurities, such as the residual catalyst in the as-received BNNTs, might possibly have formed a liquid phase when the sintering temperature was increased.

As shown in Fig. 3, the BNNTs hardly suppressed the grain growth. Instead, small overall grain growth was observed with the BNNT addition, as seen in Fig. 3(c) and (d), and this is unlikely to result in the alumina-BNNT composites to be toughened by grain boundary strengthening and reduced grain size due to the BNNT addition [5].

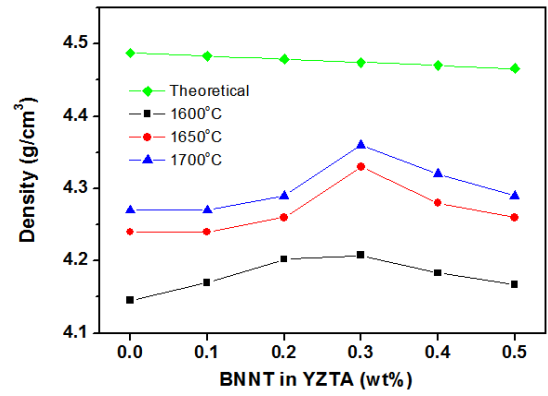


Figure 2 Sintered bulk densities of 25ZTA ceramic composites with the amount of BNNT addition and the sintering temperatures.

From this result, the BNNTs might have a different influence on the sintering behaviour of alumina-based ceramic composites; i.e., BNNTs with high purity may suppress the grain growth of the alumina matrix, while low-purity BNNTs may not suppress or may even slightly promote the grain growth due to the liquid phase formation induced by impurities such as a residual catalyst used in the BNNT synthesis process.

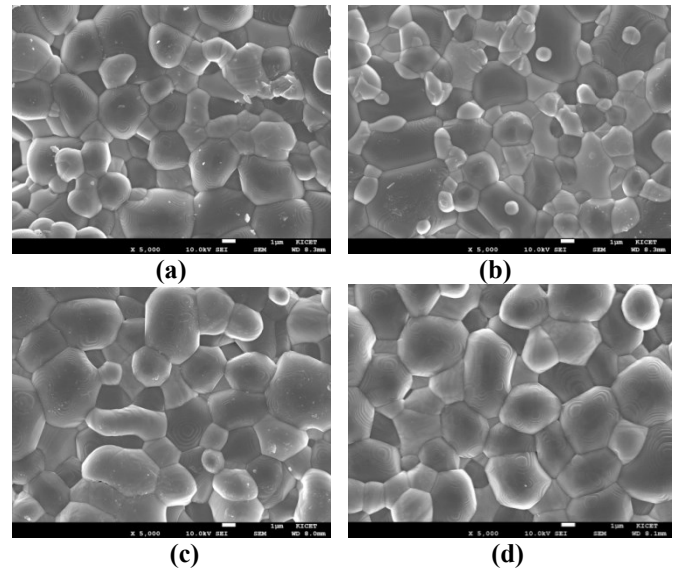


Figure 3 Microstructural evolutions of sintered 25YZTA-BNNT composite ceramics specimens with the amount of BNNT addition: (a) 25YZTA, (b) 0.1 wt% BNNT, (c) 0.3 wt% BNNT, and (d) 0.5 wt% BNNT.

Figure 4(a) shows a FE-SEM micrograph of the cross-sectional view of the fracture surface of 25YZTA-0.5wt% BNNT powder mixture in a pressed compact before sintering. Large alumina particles, fine 3YSZ particles, and entangled nano sized BNNTs are observed. The secondary electron image of the fracture surface for the sintered 25ZTA-BNNT composite sample is shown in Fig. 4(b). The BNNTs locate at the triple junction, grain boundary region, and bridges the YSZ

grain particles. The BNNT phase mainly exists in the 3YSZ grain region. The smaller size 3YSZ nano powders can be entangled easily with the BNNTs during the mixing of the starting raw powders and during the sintering process, due to more active grain growth of the 3YSZ fine powders than the relatively coarse alumina powders. The addition of BNNTs improved the flexural strength of 25YZTA up to 609 MPa when 0.3 wt% BNNT was added and sintered at 1,650°C. The details of mechanical properties will be presented separately.

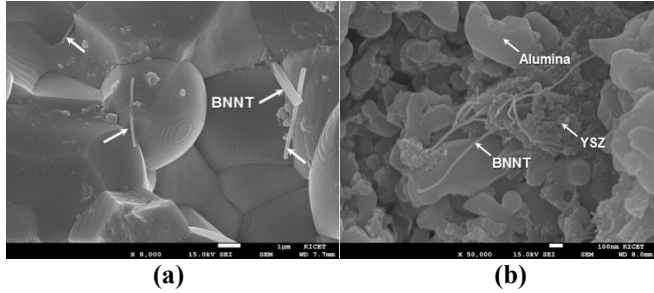


Figure 4 FE-SEM microstructures of 25ZTA-BNNT composites: (a) before sintering, (b) after sintering.

The effect of the BNNT additions to the 25YZTA ceramic on the thermal properties was investigated as shown in Fig. 5. The variation of the thermal diffusivities in Fig. 5(a) was very similar to the variation of the densities as shown in Fig. 2. Meanwhile, the specific heats of the 25YZTA-BNNT composites decreased linearly with the addition of BNNT. As a result, the thermal conductivities, that calculated from the multiplication of measured thermal diffusivity, density and the specific heat of the samples, increased slightly with the addition of BNNTs up to 0.3 wt% to the 25YZTA matrix then decreased with further addition of BNNTs as shown in Fig. 6. The maximum thermal conductivity of the 0.3 wt% BNNTs added to 25YZTA sintered at 1,650°C was 21.4 W/m·K. The degree of thermal conductivity enhancement with the addition of BNNTs was not so obvious because the amount of BNNTs added was too small compared to the 25YZTA matrix phase. The BN nanotube phase at BNNT raw powder used in this experiment was only 60%. This would have a much lower thermal conductivity than high-purity boron nitride. The fabrication of BNNTs is known to be very difficult compared to carbon nanotubes at present, even though many processes have been developed. Especially, mass-scale fabrication of high-purity BNNTs with a high yield is still challenging [10]. The measured thermal conductivities are analysed by comparing with the arithmetic and Wiener model, Fig. 6. The arithmetic (series) [12], and Wiener model [13] for the composite with two components system can be expressed as follows:

$$\kappa = c\kappa_m + (1-c)\kappa_f \quad (2)$$

$$\kappa/\kappa_f = (1-c((1-\kappa_m/\kappa_f)/(1+\alpha\kappa_m/\kappa_f)))/(1+ac((1-\kappa_m/\kappa_f)/(1+\alpha\kappa_m/\kappa_f))) \quad (3)$$

$$\alpha = 0.5, \kappa_m < \kappa_f$$

c = proportion of matrix component (m)
 $1 - c$ = proportion of filler component (f)

κ_m, κ_f = thermal conductivity of matrix and filler component

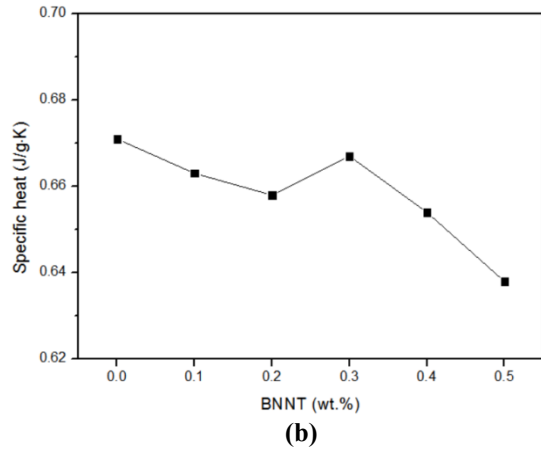
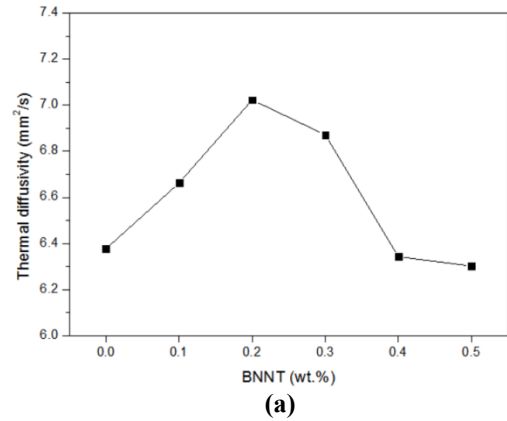


Figure 5 (a) Thermal diffusivities and (b) specific heats of 25ZTA ceramic composites with the addition of BNNT.

In this calculation, the thermal conductivities of 18.27 W/mK for 25YZTA matrix phase and 200 W/mK for BNNT filler phase was applied [14, 15]. The measured thermal conductivities of 25YZTA ceramics were slightly lower values than those calculated values by arithmetic or Wiener model at the samples with BNNTs up to 0.3 wt%. However, the measured thermal conductivities were much lower than those for theoretical model when the BNNTs added were over 0.4 wt%. This result is very similar to the thermal diffusivity data and the bulk density data as was presented in Fig. 2 and Fig. 5(a). There exists quite a large discrepancy between the experimental data and arithmetic model but the Wiener model seems quite closer to the experimental data.

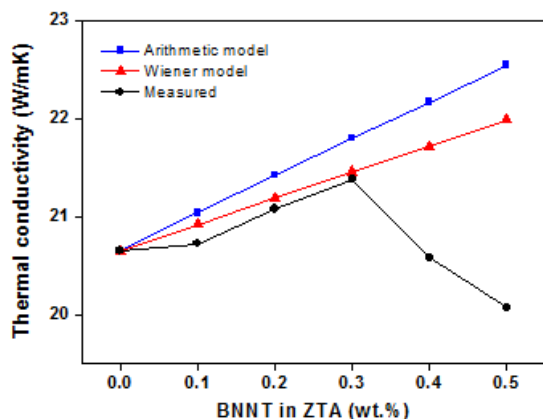


Figure 6 Measured and calculated values of thermal conductivities of 25ZTA-BNNT sintered at 1,650°C for 4h.

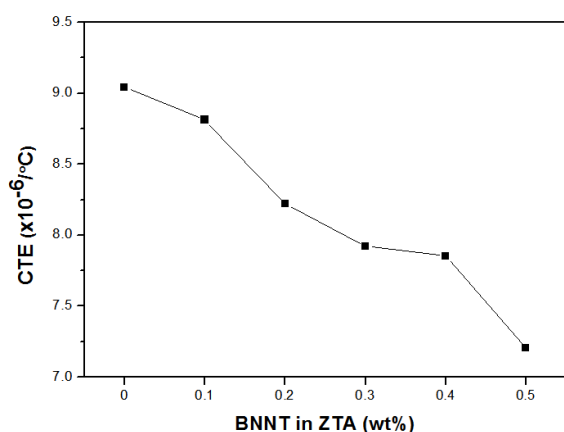


Figure 7 Variation of CTEs with the addition of BNNT into 25ZTA ceramics at the measuring temperature ranging from 25°C to 800°C.

The coefficient of thermal expansion (CTE) of 25YZTA-BNNT composites that measured at the high temperature ranging 25~800°C in air atmosphere are plotted in Figure 7. The heating rate was 10°C/min. It was found that the CTE decreased with the amount of BNNT in 25ZTA increased. The CTE of pure 25YZTA at a given temperature range was 9.04 ppm/°C, but it was decreased to 7.21 ppm/°C when BNNT of only 0.5 wt% was added. In general, the CTE of alumina ceramics increases with increasing measuring temperatures. The CTE of boron nitride material is 0.3~1 ppm/°C, and that of zirconia or yttria stabilized zirconia is 9~11 ppm/°C. Therefore, the addition of BNNT suppressed the thermal expansion of 25YZTA at high temperature and thus greatly improved the thermal stability up to 800°C.

Overall, the thermal conductivities of 25YZTA-BNNT composite ceramics depended on the amount of BNNT addition and the sintered bulk density of the composites. The addition BNNTs to the 25YZTA ceramics resulted in minor improvement in thermal conductivity but greatly decreased the

CTEs at high temperature range thereby enhancing the high temperature thermal stability up to 800°C.

CONCLUSION

Zirconia toughened alumina composite ceramics containing small amounts of boron nitride nanotubes, ZTA-BNNT, were developed and had enhanced mechanical strength and thermal conductivity compared to conventional ZTA ceramics. Small amounts of BNNTs, up to 0.5 wt%, were added to the alumina-based composite ceramics containing 25 vol% of 3 mol% yttria-stabilized zirconia, 25YZTA. The thermal conductivity of the same sample exhibited a minor increase, from 20.7 to 21.4 W/m-K, due to the low BN content in the BNNTs. However, the addition of BNNT enabled the flexural strength of 25YZTA composites sintered at 1,650°C up to 609 MPa when 0.3 wt% BNNT was added. The thermal conductivities of 25YZTA-BNNT composite ceramics depended on the amount of BNNT addition and the sintered bulk density of the composites. The addition BNNTs to the 25YZTA ceramics resulted in minor improvement in thermal conductivity but decreased the CTE at high temperature, which may have a potential for applications in the ceramic packages with thin profile and enhanced heat dissipation.

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REFERENCES

- [1] Miric A., and Dietric P., Inorganic substrates for power electronics applications, Heraeus Deutschland GmbH and Co., KG 63450 Hanau Germany, March 2015.
- [2] Liu S., and Luo X.B., LED packaging for lighting applications: design, manufacturing and testing. *Wiley and Chemical Industry Press*, 2011, ISBN: 978-0-470-82783-3.
- [3] Munro R.G., Evaluated material properties for a sintered α -alumina, *J. Am. Ceram. Soc.*, Vol. 80, No. 8, 1997, pp. 1919-1928.
- [4] Wang J., and Stevens R., Zirconia-toughened alumina (ZTA) ceramics, *J. Mater. Sci.*, Vol. 24, No.10, 1989, pp. 3424-3440.
- [4] Ferreira T.H., Silva P.R.O., Santos R.G., and Sousa E.M.B., A novel synthesis route to produce boron nitride nanotubes for bioapplications, *J. Biomater. Nanobiotechnol.*, Vol. 2, 2011, pp. 426-434.
- [5] Huang Q., Bando Y., Yu X., Nishimura T., , Zhi C., Tang C., Xu F., Gao L., and Golberg D., Enhancing superplasticity of engineering ceramics by introducing BN nanotubes, *Nanotechnology*, Vol. 18, 2007, 485706 (7pp), doi: 1088/0957-4484/18/48/485706.
- [6] Wang W.L., Bi J.Q., Sun K.N., Du M., Long N.N., and Bai Y.J., Thermal shock resistance behaviour of alumina ceramics incorporated with boron nitride nanotubes, *J. Am. Ceram. Soc.*, Vol. 94, No. 8, 2011, pp. 2304-2307.

- [7] Wang W.L., Bi J.Q., Wang S.R., Sun K.N., Du M., Long N.N., and Bai Y.J., Microstructure and mechanical properties of alumina ceramics reinforced by boron nitride nanotubes, *J. Eur. Ceram. Soc.*, Vol. W31, 2011, pp. 2277-2284.
- [8] Xu J.J., Bai Y.J., Wang W.L., Wang S.R., Han F.D., Qi Y.X., and Bi J. Q., Toughening and reinforcing zirconia ceramics by introducing boron nanotubes, *Mater. Sci. Eng., A*, Vol. **546**, 2012, 301-306.
- [9] Tatarko P., Grasso S., Chlup Z., Porwal H., Kasiarova M., Dlouhy I., and Reece M.J., Toughening effect of multi-walled boron nitride nanotubes and their influence on the sintering behaviour of 3Y-TZP zirconia ceramics, *J. Eur. Ceram. Soc.*, Vol. 34, 2014, pp. 1829-1843.
- [10] Singhal S.K., Srivastava A.K., Singh B.P., and Gupta A.K., synthesis and characterization of boron nitride nanotubes using a simple chemical method, *Indian J. Eng. Mater. Sci.*, Vol. 15, No. 10, 2008, pp. 419-424.
- [11] Naga S.M., Bondioli F., Fino P., and Hassan A.M., Thermal diffusivity of ZTA composites with different YSZ quantity, *J. Alloys and Comp.*, Vol. 695, Feb., 2017, pp. 1859-1862.
- [12] Progelhof R.C., Throne J.L., and Ruetsch R.R., Methods for predicting the thermal conductivity of composite systems: A review," *Polym. Eng. Sci.*, Vol. 16, 1976, pp. 615-625.
- [13] Wiener O., "Die theorie des mischkörpers für das feld der stationären strömung: 1," *Leipzig: B. G. Teubner.*, Vol. 32, 1912, pp. 507-604.
- [14] Buntebarth G., and Schopper J.R., "Experimental and theoretical investigations on the influence of fluids, solids and interactions between them on thermal properties of porous rocks," *Phys. Chem. Earth.*, Vol. 23, 1998, pp. 1141-1146.
- [15] Jakubinek M.B., Niven J.F., Johnson M.B., Ashrafi B., Kim K.S., and White M.A., Thermal conductivity of bulk boron nitride nanotube sheets and their epoxy-impregnated composites, *Phys. Status Solidi A.*, Vol. 213, 2016, pp. 2237-2242.