Densification and Thermo-Mechanical Properties of Al$_2$O$_3$-ZrO$_2$ (Y$_2$O$_3$) Composites

Hee Seung Kim, Mi Young Seo, and Ik Jin Kim*[†]

Institute of Advanced Ceramics for Semiconductor in BIEMT Co. LTD., Chungnam 336-864, Korea
**Institute for Processing and Application of Inorganic Materials (PAIM),*
Department of Materials Science and Engineering, Hanseo University, Chungnam 356-706, Korea
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ABSTRACT

The microstructure of ZrO$_2$ toughened Al$_2$O$_3$ ceramics was carefully controlled so as to obtain dense and fine-grained ceramics, thereby improving the properties and reliability of the ceramics for capillary applications in semiconductor bonding technology. Al$_2$O$_3$-ZrO$_2$(Y$_2$O$_3$) composite was produced via Ceramic Injection Molding (CIM) technology, followed by Sinter-HIP process. Room temperature strength, hardness, Young's modulus, thermal expansion coefficient and toughness were determined, as well as surface strengthening induced by the fine grained homogenous microstructure and the thermal treatment. The changes in alumina/zirconia grain size, sintering condition and HIP treatment were found to be correlated.

Key words : ZTA (Zirconia Toughened Alumina), Hardness, Young's modulus, Toughness, Bonding capillary

1. Introduction

Zirconia Toughened Alumina (ZTA) is one of the most widely used advanced ceramics for bonding capillary technology because of its excellent physical and thermo-mechanical properties.[1,2] ZTA has considerably higher strength and toughness than alumina. This is the result of the stress-induced transformation toughening achieved by the incorporating of fine zirconia particles uniformly throughout the alumina. Previous studies have demonstrated that a desired microstructure can be achieved through the addition of 20 wt% YSZ, which acts as a second-phase pinning agent.[3,4] Technology for semiconductor components integration is rapidly advancing to a level previously not thought possible. Furthermore, high integration demands both existing manufacturing precision and high product reliability at low cost.[5,6] In this work, the microstructure evolution of ceramic composites and its correlation with important criteria in the selection of a suitable capillary material of ZTA ceramics for a specific package application are discussed.

2. Experimental Procedure

Commercially available Al$_2$O$_3$ (99.5%, Alcoa A-16), and ZrO$_2$ (95.0%, 3 mol% yttria stabilized tetragonal zirconia, Junsei Co.) were used as starting powders. The average particle size of Al$_2$O$_3$ was approximately 0.65~0.70 μm and the major

impurities included SiO$_2$, Fe$_2$O$_3$, Na$_2$O, and CaO etc. Up to 10~20 wt% of ZrO$_2$ (0.1~0.3 μm) was added to the Al$_2$O$_3$, and this mixture was ball milled for 48 h using distilled water and zirconia balls as media. After drying and sieving, the mixtures were injection molded with a binder of 15~20% and sintered at 1100~1560°C for 2 h. The sintered samples were HIP treated under 1400°C/1000 bar using Ar gas. The microstructure of the specimens was observed by SEM/EDX (JEOL, JSM-5600/ISIS 300) after chemical and thermal etching of the polished surface. Grain size distribution was measured using an image analyzer (Sigma Scan. Pro.5). The composition and morphology of individual grains were observed by X-ray diffraction (Rigaku, D/Max 2200 Ultima, Ni-filtered CuKα) and Scanning Electron Microscopy (SEM, JSM-5600, JEOL). The thermal expansion coefficient from Room Temperature (RT) to 1350°C was determined for a bar specimen in air using a dilatometer (Linseis, L76), at a heating rate of 10 K min^{-1} and a cooling rate of 10 K min^{-1}. The strength was measured using a four-point bending configuration (Instron, 8801) with a cross-head speed of 0.5 mm/min and inner and outer spans of 10 and 20 mm, respectively. The elastic modulus of the specimens was measured by the ultrasonic method using a bending strength sample. The hardness profile was determined primarily by measuring the hardness of the polished surface of the specimen. The fracture toughness was measured by the indentation-strength method using the Anstis formula.[7]

3. Results and Discussion

3.1. Densification and Grain Size
The variation of relative density of ZTA and the grain size

[†]Corresponding author : Ik Jin Kim
E-mail : ijkim@hanseo.ac.kr
Tel : +82-41-660-1441   Fax : +82-41-688-4143

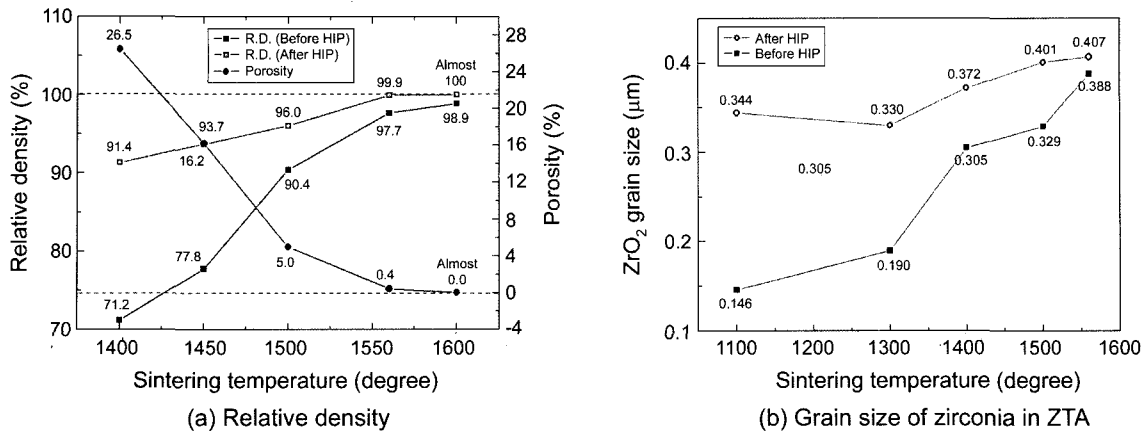(a) Relative density

(b) Grain size of zirconia in ZTA

Fig. 1. The relative density and zirconia grain size of ZTA as a function of heat treatment.

of zirconia in ZTA with sintering and HIP treatment temperature are shown in Fig. 1(a) and (b), respectively. It can be seen that the relative density and the zirconia grain size of the as-sintered samples increased with sintering temperature and HIP treatment. The relative density of ZTA and the zirconia in ZTA sintered at 1560°C for 2 h were 97.7% and 0.39 µm, respectively, as shown in Fig. 1(a) and (b). The relative density of ZTA and the grain size of zirconia in ZTA treated by HIP (1400°C, 1000 bar) after sintering at 1560°C for 2 h were 99.9% and 0.41 µm, respectively. As expected, the grain size of zirconia in ZTA increased with the sintering temperature increment and HIP treatment.

In general, the effect of HIP-post-densification on the microstructure of ceramics included the elimination of residual pores, the healing of small surface cracks and the

elimination of an agglomerate-induced sintered microstructure with inter- and intra-agglomerate porosity. However, it has been shown that grain growth at excessive HIP temperature results in a degradation of strength.[8] In the case of zirconia-based ceramics, the mechanical properties depend not only on the density but on the microstructure uniformity of the sintered sample.[9]

3.2. Microstructure

The microstructure analysis of ZTA materials revealed that zirconia grains in ZTA are more evenly distributed on the grain corners of the Al_2O_3 matrix, as shown in Fig. 2(a), (b), and (c). The zirconia grain in ZTA remained inter-granular for all sintering conditions. Both the zirconia and Al_2O_3 grains coarsened during the heat treatment, however: only

(a) Sintered at 1500°C for 2 h

(b) Sintered at 1560°C for 2 h

(c) HIP treatment after sintered 1560°C for 2 h

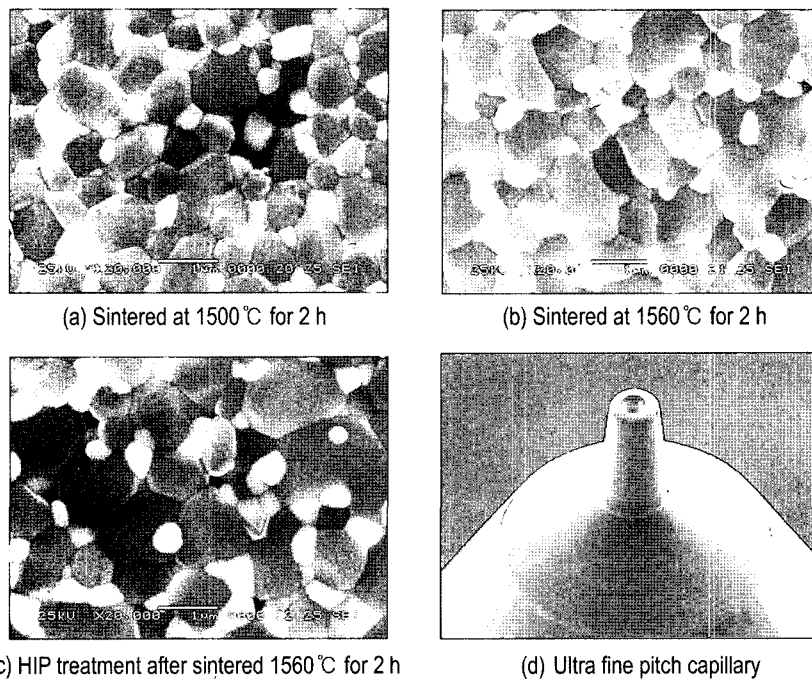(d) Ultra fine pitch capillary

Fig. 2. Microstructure of ZTA sintered at 1500°C/2 h (a), ZAT sintered at 1560°C/2 h (b), HIP treated ZTA (1560°C/2 h) at 1400°C/1000 bar (c), and ultra-fine pitch capillary (d).

Table 1. Physical and Thermal Properties of Pure ZrO_2, Al_2O_3, and ZTA (ZrO_2-Al_2O_3) Sintered at 1560°C for 2 h, and HIP Treated at 1400°C/1000 bar

Materials	Density [g/cm³] (Relative density)	Grain size [μm]	Elastic modulus [GPa]	Hardness [Hv]	K_{1C} [MPa·m$^{1/2}$]	Thermal expansion coefficient [×10⁻⁶/K]	Brittleness [μm⁻¹/²]
ZrO_2	5.89	0.30	200	1300	6~12	10~11	2.16
Al_2O_3	3.98	1.0~1.5	400	2000	3.5 ~ 4.4	6.5~9.5	6.17
ZTA	4.12 (97%)	0.388	279	1980	5.2	9.6	3.49
ZTA*	4.27 (99.9%)	0.391	285	1875	5.8	9.5	3.01

* : HIP treated sample, ( ) : relative density

the grain size changed, while the ratio of alumina/zirconia grain sizes was unchanged. In general, the zirconia grain prevents the grain growth of Al_2O_3 grain during coarsening. The zirconia grains are ripened by coalescence, in this process, and the zirconia grain at Al_2O_3 corners are dragged by migrating Al_2O_3 boundaries and meet other zirconia grain as the Al_2O_3 grain edges and face disappear.[9] All the specimens of ZTA sintered at 1600°C before and after HIP treatment had greater than 99% of theoretical density and zero level porosity, as shown in Fig. 1(a). By increasing the sintering temperature, from 1100 to 1560°C, the grain size of zirconia increased from 0.146 to 0.39 μm. The Fig. 2(d) shows the tip of an ultra-fine pitch capillary, which has the same microstructure as that shown in Fig. 2(c). After sintering at 1560°C for 2 h and fine manufacturing, the capillaries were hot pressed with an applied pressure of 1000 bar in argon at 1400°C for 1 h.

3.3. Mechanical and Thermal Properties

The mechanical properties, hardness and elastic modulus of the specimens are listed in Table 1. In all cases the indentor were aligned so that their diagonals and possible radial cracks were parallel and perpendicular to the composite layers. The size of the indents and the crack lengths were measured via optical microscope. Indentation fracture toughness (K_{IC}) was calculated from the length of the cracks induced by the same indents using the Anstis formula (1)

$$K_{IC} = \eta(E/H)^{1/2}P/c^{3/2} \qquad (1)$$

where η is a geometric factor estimated as 0.016, E is the modulus of elasticity, H is the hardness, P is the indentation load, and c is the indentation radial crack half-length at the surface. Here, the c values were the lengths of the cracks parallel to the layers only because these were not influenced by the in-plane residual stresses.

The hardness and the elastic modulus of ZTA were also increased with the addition of 20 wt% of ZrO_2 as was the fracture toughness. The relative increase in toughness of ZTA due to transformation-toughening critically depends on the transformation temperature and the grain size of dispersed zirconia in the alumina matrix. In general, the hardness of ceramic materials is a critical property as it relates to the ability of the material to withstand penetration of the surface through a combination of brittle fracture and plastic

flow. Factors that need to be taken into account when interpreting hardness data for ceramic materials are the amount of porosity in the surface, the grain size of the microstructure and the effects of grain boundary phases.[10]

4. Conclusions

Fine grained and well-dispersed homogenous microstructure of ZTA ceramics was synthesized by ceramic injection molding, followed by a Sinter-HIP process. The relative density and grain size zirconia in ZTA treated by HIP (1400°C, 1000 bar) after sintering at 1560°C for 2 h were 99.9% and 0.41 μm, respectively. The effect of HIP-post-densification on the microstructure of the ceramics include the elimination of residual pores, the healing of small surface cracks and the elimination of an agglomerate-induced sintered microstructure with inter- and intra-agglomerate porosity. However, grain growth at excessive HIP temperature results in a degradation of mechanical properties.

Acknowledgment

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