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Effect of Cr_2O_3 Content on Densification and Microstructural Evolution of the Al_2O_3-Polycrystalline and Its Correlation with Toughness

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ABSTRACT

The effects of Cr_2O_3 on the microstructural evolution and mechanical properties of Al_2O_3 polycrystalline were investigated. The microstructure of Al_2O_3-Cr_2O_3 composites (ruby) was carefully controlled in order to obtain dense and fine–grained ceramics, thereby improving their properties and reliability with respect to numerous applications related to semiconductor bonding technology. Ruby composites were produced by Ceramic Injection Molding (CIM) technology. Room temperature strength, hardness, Young's modulus and toughness were determined, as well as surface strengthening induced by thermal treatment and production of a fine-grained homogenous microstructure.

Key words ***:*** ***Al_2O_3-Cr_2O_3 composites, Ruby, Microstructure, Injection molding, Toughness***

1. Introduction

Among advanced ceramics for bonding capillary technology, Al_2O_3-Cr_2O_3 composites (ruby) are a good candidates for ultra long life capillary due to its excellent physical and thermo-mechanical properties. In general, polycrystalline ruby ($Al_2O_3+Cr_2O_3$) is a translucent alumina ceramic that acquires a distinctive red color from Cr_2O_3 where about 1% of Al^{3+} is replaced by Cr^{3+}. Polycrystalline ruby is inert, biocompatible, and it resists wear, heat and acids. It is considerably higher in strength and toughness than alumina.[1,2] The impact of Cr_2O_3 on the mechanical properties of Al_2O_3 ceramics is now well established; it increases the hardness, strength, and thermal shock resistance of Al_2O_3. These improvements are believed to be closely related to changes in microstructure.[3] Rapid migration of the grain boundaries due to the coherency strain energy was proposed as a possible mechanism for the changes in the microstructure.[4,5] Furthermore, there have been many studies have focused on controlling the microstructure of Al_2O_3 polycrystalline by the addition of second phases, such as Cr_2O_3, TiO_2, MnO_2, and combinations of other oxides.[6] In the present study, the microstructural evolution and the effect of Cr_2O_3 on the mechanical properties of Al_2O_3-containing Cr_2O_3 up to 0.5~2.0 wt% are investigated.

2. Experimental Procedure

Commercially available Al_2O_3 (99.5%, Alcoa A-16) and Cr_2O_3 (99.8%, Kanto Co.) were used as starting powders. The average particle size of Al_2O_3 was in the range of 0.65~0.7 μm and the major impurities were SiO_2, Fe_2O_3, Na_2O, and CaO, among others. Up to 0.5~2.0 wt% of Cr_2O_3 (0.2~0.8 μm) was added to the Al_2O_3 and ball milled for 24 h using distilled water and zirconia balls as media. After drying and sieving, the mixtures were injection molded with 15~20% binders and sintered at 1400~1560°C for various periods of time. All of the sintered samples were HIP treated under conditions of 1400°C/1000 bar in argon. The grain size distribution was measured using an image analyzer (Sigmascan Pro 5). The microstructure of the specimens was observed by SEM/EDX (Jeol, JSM-5600/ISIS 300) after chemical and thermal etching of the polished surface. The strength was measured using a four-point bending configuration (Instron) 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 an ultrasonic method using the bending strength sample. The hardness was primarily measured across the polished surface of the specimen primarily in order to determine the hardness profile. Indentations were made using a micro-indentor with an applied load of 1 kg. The fracture toughness was measured by the indentation-strength method using the Anstis formula.[7] In all cases the indentor was aligned such that the diagonals and possible radial cracks of the specimens were parallel or perpendicular to the composites. The size of the indents and the crack lengths were mea-

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sured using an 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, as these are not influenced by the in-plane residual stresses.

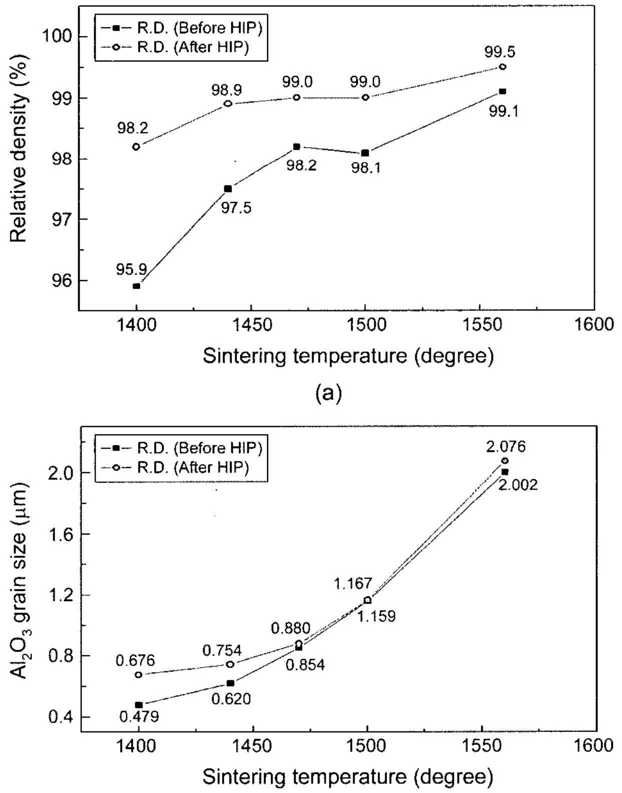
3. Results and Discussion

3.1. Densification and Grain Size

The variation of relative density and grain sizes of Al_2O_3-Cr_2O_3 polycrystalline after the sintering and HIP treatment temperature are shown in Fig. 1(a) and (b), respectively. It is clear that the grain size of the as-sintered samples increased with sintering and with the HIP treatment temperature increment. Even with a low sintering temperature of 1400°C, the Al_2O_3-Cr_2O_3 shows a nearly full densification with a relative density of 95.9% and has the Al_2O_3 grain size of 0.478 μm. The relative density of this sample under the HIP treatment at 1400°C/1000 bar is 98.2%, as indicated in Fig. 1(a). The ruby composites can be sintered to a nearly full density (>99.1%) at approximately 1470°C for 2 h. As expected, the grain size of the Al_2O_3 in ruby increases with the HIP treatment temperature, as shown in Fig. 1(b). In general, the effect of HIP-post-densification of the microstructure of the ceramics results in 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, the grain-growth at excessive HIP temperature results in a degradation of strength.[8] The HIP-treated sample with the higher relative density of 99.5% shows better mechanical properties. For Al_2O_3-based ceramics, the mechanical properties not only depend on the density but also depend on the microstructural uniformity of the sintered sample.[9]

3.2. Microstructure

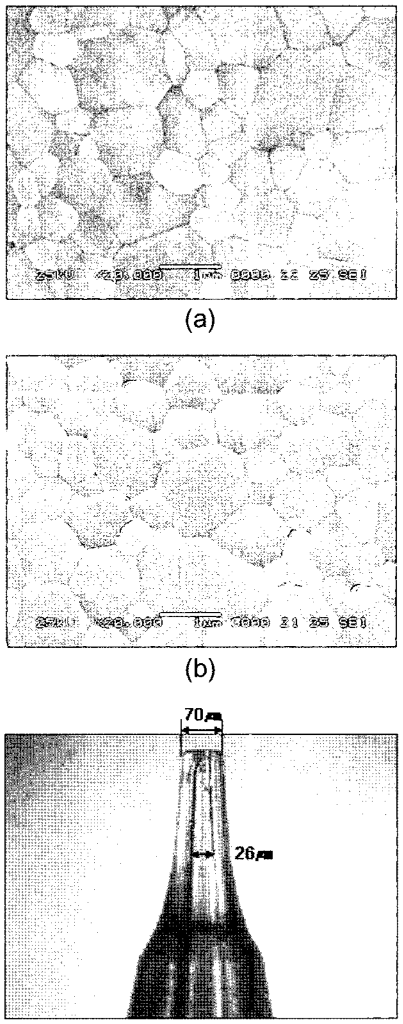
The microstructure of the ruby indicates that all the grains have angular shapes, as shown in Fig. 2. As the sin-



(a)

(b)

Fig. 1. Relative density (a) and grain size (b) of the Al_2O_3-Cr_2O_3 (ruby, 1.0 wt%Cr_2O_3) as a function of heat treatment.



(a)

(b)

(c)

Fig. 2. Microstructure of Al_2O_3-1.0 wt% Cr_2O_3 (ruby) sintered at 1400°C/2 h (a), HIP-treated ruby (1400°C/2 h) at 1400°C/1000 bar (b), and transparent ruby capillary (c).

Table 1. Mechanical Properties of Al_2O_3-Cr_2O_3 Composites (1470°C for 2 h), HIP Treated at 1400°C/1000 bar in Argon

Materials	Density [g/cm^3]	Grain size [μm]	Elastic Modulus [GPa]	Hardness [H_{v10}]	K_{1C} [MPa·m$^{1/2}$]	Brittleness [μm$^{-1/2}$]
Al_2O_3	3.98	1.0~1.5	400	2100	3.4	6.17
Al_2O_3-0.5 wt%Cr_2O_3	3.980	0.758	402.5	1915	5.22	3.61
Al_2O_3-1.0 wt%Cr_2O_3	3.980	0.880	403.5	1914	5.30	3.66
Al_2O_3-1.5 wt%Cr_2O_3	3.982	0.898	392.2	1900	5.06	3.52
Al_2O_3-2.0 wt%Cr_2O_3	3.985	0.935	393.2	1818	5.12	3.58

tering temperature increases under the same conditions, the size of the grains increases larger and a grain sizes of up to 0.85 μm at 1470°C for 2 h and as high to as 0.88 μm after HIP treatment at 1400°C/1000 bar in argon, respectively, are observed, respectively. All of the specimens of ruby sintered at 1470°C before and after the HIP treatment previously had theoretical density higher than 98.90% and had a zero-level porosity. The grain size of the pure Al_2O_3 was 1.0~1.5 μm under sintering at 1470°C for 2 h, followed by HIP treatment at 1400°C/1000 bar in argon. As the amount of Cr_2O_3 was increased from 0.5 wt% to 2.0 wt%, the size of grains increased from 0.76 μm to 0.93 μm, as shown in Table 1. The hardness and the elastic modulus of Al_2O_3-Cr_2O_3 composites increased by the addition of 0.5~1.0 wt% Cr_2O_3 due to the well controlled grain size. Similar to the case of elastic modulus, the fracture toughness also improved when a small amount (0.5~1.0 wt%) of Cr_2O_3 was added.

3.3. Mechanical and Thermal Properties

The mechanical properties, hardness, elastic modulus and toughness of the specimens with different amounts of Cr_2O_3 are listed in Table 1.

The elastic modulus of Al_2O_3-Cr_2O_3 was also improved with the addition 1.0 wt% of Cr_2O_3 as was the case of the fracture toughness. However, the hardness rating was decreased. The fracture toughness of Al_2O_3 has been previously observed to increase when the average grain size becomes larger. The formation of large elongated or platelike grains was also reported to increase the fracture toughness of the material.[10,11] In both cases, bridging of the propagating cracks by large grains was responsible for these increase. In this work, the average grain size increased and the platelike grains as well as the matrix grains may play a major role in increasing the fracture toughness.

4. Conclusions

The microstructure of Al_2O_3-Cr_2O_3 composites (ruby) was carefully controlled in order to obtain dense and fine-grained ceramics by Ceramic Injection Molding (CIM) technology and a HIP treatment. The relative density of the sample sintered at 1470°C for 2 h under the HIP treatment at 1400°C/1000 bar was greater than 99.0%. As the sintering temperature increased and with increased Cr_2O_3 content (1.0 wt%), the size of the grains increased the grains up to 2.076 μm. The average grain size of Al_2O_3-Cr_2O_3 composites increased with increasing Cr_2O_3 content. Platelike grains in addition to matrix grains may play a major role in increasing the fracture toughness. The elastic modulus, the hardness, and also the fracture toughness were remarkably improved by the addition of small amounts (0.5~1.0 wt%) of Cr_2O_3.

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