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学 位 論 文 の 概 要 及 び 要 旨

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題　　目 Microstructure and mechanical properties of in-situ synthesized Al_2O_3/Ba-β-Al_2O_3/ZrO_2 composites（In-situ 合成した Al_2O_3/Ba-β-Al_2O_3/ZrO_2 複合材料の組織と機械的性質）

学位論文の概要及び要旨

Al_2O_3 is one of the most widely used ceramic materials because of its high strength and hardness, excellent heat and wear resistance. Nevertheless, the large-scale applications of monolithic Al_2O_3 ceramic are very limited due to its relatively low fracture toughness. Compared to direct additions of fibers and whiskers, the incorporation of elongated reinforcements with high aspect ratios through in-situ reactions has advantages of reducing processing costs, as well as obtaining denser and more homogeneous microstructure.

Chapter 1 described the background of the present research. In order to improve the fracture toughness of monolithic Al_2O_3 ceramic, a combination of crack deflection, crack bridging, and martensitic transformation of ZrO_2 from tetragonal to monoclinic phase was proposed to fabricate Al_2O_3/Ba-β-Al_2O_3/ZrO_2 composites.

In Chapter 2, Al_2O_3/Ba-β-Al_2O_3/ZrO_2 composites were fabricated by solid-state reaction sintering of Al_2O_3, $BaZrO_3$, and 3 mol% yttria-stabilized zirconia (3YSZ) powders. The effects of YSZ addition on microstructure and mechanical properties have been investigated. The incorporation of YSZ promoted the densification of the composites and formation of tetragonal ZrO_2 phase. The microstructure of the composites was characterized by elongated Ba-β-Al_2O_3 phase and equiaxed ZrO_2 particles including added YSZ and reaction-formed ZrO_2. The Al_2O_3/Ba-β-Al_2O_3/ZrO_2 composites with YSZ addition exhibited improved fracture toughness, as a result of multiple toughening effects including crack deflection, crack bridging, crack branching, and martensitic transformation of ZrO_2 formed by the reactions between Al_2O_3 and $BaZrO_3$. Moreover, owing to the grain refinement of Al_2O_3 matrix, dispersion strengthening of the added YSZ particles, and an increase in density of the composites, the Vickers hardness and flexural strength of Al_2O_3/Ba-β-Al_2O_3/ZrO_2 composites were dramatically enhanced in comparison with the composites without YSZ addition.

In Chapter 3, Al_2O_3 matrix composites containing in-situ formed monoclinic zirconia (m-ZrO_2) and Ba-β-Al_2O_3 were prepared via reactive sintering of Al_2O_3 and $BaZrO_3$ powders. To improve the fracture toughness of Al_2O_3/Ba-β-Al_2O_3/m-ZrO_2 composites, YSZ with different Y_2O_3 contents (1.5YSZ, 2YSZ, and 3YSZ) and Y_2O_3 particles were introduced into Al_2O_3 and $BaZrO_3$ powder mixtures, and the effect of YSZ or Y_2O_3 addition on densification behavior,

microstructure, and mechanical properties of Al_2O_3/Ba-β-Al_2O_3/ZrO_2 composites has been investigated. The reaction-formed *m*-ZrO_2 was transformed into tetragonal ZrO_2 (*t*-ZrO_2), resulting from the migration of Y^{3+} from YSZ or Y_2O_3. The incorporation of YSZ particles contributed to the refinement of Al_2O_3 grains, whereas Y_2O_3-added samples showed larger grain sizes of Al_2O_3 matrix. The Al_2O_3/Ba-β-Al_2O_3/ZrO_2 composites with YSZ or Y_2O_3 addition exhibited high fracture toughness, which is attributed to crack deflection/bridging and $t \rightarrow m$ transformation toughening. Although the phase transformation is mainly derived from ZrO_2 formed during sintering, 1.5YSZ particles added in the composites still showed much higher phase transformability compared to 2YSZ and 3YSZ particles.

In Chapter 4, Al_2O_3/Ba-β-Al_2O_3/ZrO_2 composites were prepared by solid-state reaction sintering of high-energy ball-milled Al_2O_3–$BaZrO_3$ powder mixtures and YSZ nanopowder. The powder characterization of Al_2O_3 and $BaZrO_3$ powders as well as sintering behavior and microstructure of Al_2O_3/Ba-β-Al_2O_3/ZrO_2 composites were investigated. After high-energy ball-milling (HEBM) for 48 h, the particle size of $BaZrO_3$ was significantly reduced. However, no evident particle refinement of Al_2O_3 occurred. The Ba-β-Al_2O_3 phase presented a more equiaxed morphology instead of platelet structure, which enhanced the densification of the composites. Al_2O_3/Ba-β-Al_2O_3/ZrO_2 composites sintered at 1500 °C, based on powders ball-milled for 72 h, presented the highest Vickers hardness of 17.3 GPa. Meanwhile, the composites sintered at 1600 °C, based on powders without HEBM, presented the highest fracture toughness of 4.3 MPa $m^{1/2}$.

In Chapter 5, to improve the mechanical properties and thermal shock resistance of zirconia toughened alumina (ZTA) composites, $BaCO_3$ was added to YSZ and Al_2O_3 powders to form ZTA/Ba-β-Al_2O_3 composites, which were prepared by a solid-state reactive sintering method. As $BaCO_3$ content increased, more Ba-β-Al_2O_3 was formed, resulting in the decreases in relative density and Vickers hardness. The fracture toughness was enhanced with increasing $BaCO_3$ content and reached a peak at 4 wt% $BaCO_3$. The improved fracture toughness is the result of synergistic toughening effects of martensitic transformation of ZrO_2 and crack deflection/bridging. After thermal shock tests, the residual strength of ZTA/Ba-β-Al_2O_3 composites was higher than that of ZTA. The improvement in thermal shock resistance is mainly ascribed to the formation of elongated Ba-β-Al_2O_3 with a hexagonal structure, which can dissipate the energy associated with crack propagation during thermal shock.

In Chapter 6, calcium hexaaluminate ($CaAl_{12}O_{19}$ or CA_6) ceramics were fabricated by reactive sintering of Al_2O_3 and $CaCO_3$ powder mixtures. The influence of Ti^{4+} doping on microstructural development of CA_6 ceramics was investigated. The doped Ti^{4+} led to formation of Al vacancies (V_{Al}) in mirror planes of CA_6 by replacing Al^{3+}, resulting in promotion of crystal growth of CA_6 along *c* axis and thus the decrease in aspect ratios of CA_6 grains. Meanwhile, Al_2O_3 and $CaTiO_3$ were also formed in Ti^{4+}-doped samples.

In Chapter 7, some general conclusions of this work were made. In addition, a few schedules to motivate the future research were also proposed.