THE EFFECTS OF CR_2O_3 ADDITION ON MICROSTRUCTURE AND FRACTURE TOUGHNESS OF ZTA CERAMIC COMPOSITE

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ABSTRACT

The microstructure and mechanical properties of ceramic composites produced from alumina, yttria stabilized zirconia and chromia oxide system was investigated. The Cr_2O_3 weight percent was varied from 0 wt% to 1.0 wt%. Each batch of composition was mixed, uniaxially pressed to 13mm diameter and sintered at 1600 °C for 4 h in pressureless conditions. Studies on the effects of the sample microstructures on their mechanical and physical properties such as fracture toughness and bulk density were carried out. Results show that an addition of 0.6 wt% of Cr_2O_3 produces the best mechanical properties. Furthermore, microstructural observations show that the Al_2O_3 grain size is significantly dependent on the amount of Cr_2O_3 additives used. Maximum value obtained with 0.6 wt % Cr_2O_3 for the fracture toughness is 5.36 $MPa.m^{1/2}$.

ABSTRAK

Mikrostruktur dan ciri-ciri mekanikal komposit seramik dihasilkan dari alumia, zirkonia distabilkan yttria dan kromia telah di siasat. Berat peratus kromia dibezakan dari 0 % berat ke 1.0 % berat. Setiap kumpulan komposisi dicampur dan ditekan secara hidraulik kepada pellet berdiameter 13mm dan disinter pada 1600 °C selama 4 jam dalam keadaaan tanpa tekanan. Kajian terhadap kesan mikrostrutur terharap sifat mekanikal dan fizikal seperti keliatan patah dan ketumpatan pukal dijalankan. Keputusan menunjukkan penambahan sebanyak 0.6 % berat Cr_2O_3 menghasilkan sifat mekanikal terbaik. Tambahan pula, pemerhatian terhadap mikrostruktur menunjukkan saiz butir Al_2O_3 adalah sangat bergantung kepada amaun tambahan Cr_2O_3 yang digunakan. Keputusan tertinggi dihasilkan oleh 0.6 % berat Cr_2O_3 untuk keliatan patah ialah 5.36 $MPa.m^{1/2}$.

Keywords: ceramics, Cr_2O_3, composite materials, fracture toughness

INTRODUCTION

Advanced ceramic materials are a good candidate for cutting insert application due to its high hot hardness (Like et al., 2007). Alumina based materials are one of the potential ceramics used to fabricate cutting inserts as it has high hot hardness, high abrasion resistance and chemical inertness against the environment. Unfortunately, alumina based cutting inserts have disadvantages such as low toughness and causes failures such as chipping and breakage during machining (Azhar et al., 2009). As a result, reinforcement materials such as yttria stabilized zirconia (YSZ) (Smuk et al., 2003), titanium carbide, silver and ceria are used to improve the mechanical properties of alumina (Gatto, 2006, Dutta et al., 2006). Among other popular alumina based materials, zirconia-toughened alumina (ZTA) has been another recent addition to the group of high performance ceramics.

The ZTA composite was developed to substitute alumina ceramics in applications where a higher fracture resistance is required, for the phase transformation from the tetragonal phase to the monoclinic phase (Azhar et al., 2009, Smuk et al., 2003, Mondal et al., 1992, Casellas et al., 2003, Bansal and Choi, 2003, Sergo et al., 1998).

Even though with the reinforcement of YSZ, the properties of fracture toughness of ZTA only improved to ~4.5 $MPa.m^{1/2}$ compared to monolithic Al_2O_3; 3.9 $MPa.m^{1/2}$ (Casellas et al., 2003). Thus, the performance of a ZTA cutting insert is limited by its fracture toughness. In order to further improve ZTA cutting insert performance, the fracture toughness needs to be improved.

Chromia (Cr_2O_3) is one the many additives potentially able to improve the physical properties of alumina. When chromia is added into an alumina system, isovalent solid solution will form over the full range of compositions due to the fact that both chromia and alumina are sesquioxides and have the same corundum crystal structure (approximately hexagonal close-packed oxide ions with the Al^{3+} and Cr^{3+} ions occupying two thirds of the available octahedral intertitials sites). In reactions at high temperatures (T >1000 °C), complete ranges of substitution solid solutions are obtained (Magnani and Brillante, 2005, Bondioli et al., 2000, Zhang et al., 1997). Isovalent solid solution happens when an atom or ion replaces an atom or ion of the same charge in the parent structure. It contributes to high refractoriness and chemical stability (Bondioli et al., 2000). The addition of Cr_2O_3 also increases the hardness, tensile strength and thermal shock resistance of alumina (Riu et al., 2000). When a small amount of Cr_2O_3 (~2 mol %) is added, the grains become larger and bimodal in size distribution. At the same time, the fracture toughness and flaw tolerance of alumina are also improved. The hardness as well as elastic modulus is increased. However, fracture strength decreases with the addition of Cr_2O_3 (Riu et al., 2000).

Even though the study of ZTA and Al_2O_3–Cr_2O_3 has been done extensively for the past 20 years, the studies were carried out individually. The studied on ZTA–Cr_2O_3 as a ceramic composite system for their mechanical properties are rarely reported elsewhere, until now. In this study, the microstructural evolution and mechanical properties of Cr_2O_3 doped ZTA were investigated.

METHODOLOGY

Monolithic Al_2O_3 (average particle size 0.5μm, supplier Martinswerck, 95% purity), YSZ (average particle size 1.5μm, supplier Goodfellow, 95 % purity with Y_2O_3 as stabilizer) and Cr_2O_3 (average particle size 0.5μm, supplier Sigma-Aldrich, 99.9 % purity) were used as the starting materials. Pellets with 13mm diameter were fabricated via the solid state processing route. Samples with an 80/20 ratio for Al_2O_3/YSZ respectively were prepared with different Cr_2O_3 wt% ranging from 0 wt% to 1.0 wt%. The powders were then mixed with 0.6 wt % of polyethylene glycol 400 using a ball mill for 8 hours and pressed at 295 MPa using a hydraulic press. The specimens were then sintered in a HTF 1800 Carbolite furnace at 1600 °C for 4 hours with 5°C/min sintering rate.

Fracture toughness was calculated using the formula proposed by Niihara for Palmqvist crack (Niihara, 1983). Value for Young Modulus (E) used in this study is 310 GPa.

$$3K_{1c} = 0.035\ (Ha^{1/2})\ (3E/H)^{0.4}(l/a)^{-0.5} \qquad (1)$$

Field emission scanning electron microscopy (FESEM) was used to study the microstructure of the sintered samples. The samples were thermally etched in the same furnace used for sintering at 1400°C for 2 hours. XRD of the sintered samples was carried out to determine the phases present. The XRD patterns of the sintered products were obtained using a Bruker D8 Advanced operated in Bragg–Brentano geometry, with Cu Kα radiation, in the 10° ≤ 2θ° ≤ 90° range. Counting time was fixed at 71.5 s for each 0.03° 2θ step. The X-ray tube was operated at 40 kV and 30 mA. Quantitative phase analysis was measured by Rietveld method using HighScorePlus software. Crystal structure data for each phases present in the samples were taken from ICSD. The refinement was done in stages, with the atomic coordination and thermal parameters held fixed.

RESULT AND DISCUSSION

XRD Analysis

XRD results for the sintered ZTA-Cr_2O_3 samples are shown in Figure 1. XRD analysis indicates that Al_2O_3 was present as corundum (ICSD reference 98-001-1621). The Cr_2O_3 was in the corundum phase and matched with the ICSD reference 98-005-6901. XRD analysis also showed that YSZ has tetragonal crystal structures together with the presence of yttria (ICSD reference 98-002-0789). There is no monoclinic ZrO_2 phase observed. On the other hand, the XRD result does not detect the presence of Cr_2O_3 phase in the sample. According to the XRD analysis no new compound was formed with the addition of Cr_2O_3. Figure 2 shows the comparison of XRD results of ZTA samples with various Cr_2O_3 wt %. It is shown that the addition of Cr_2O_3 would result the monoclinic phase to disappear (shown in the red dotted box), where as the peaks for monoclinic phase are no longer seen for samples of ZTA with the addition of Cr_2O_3.

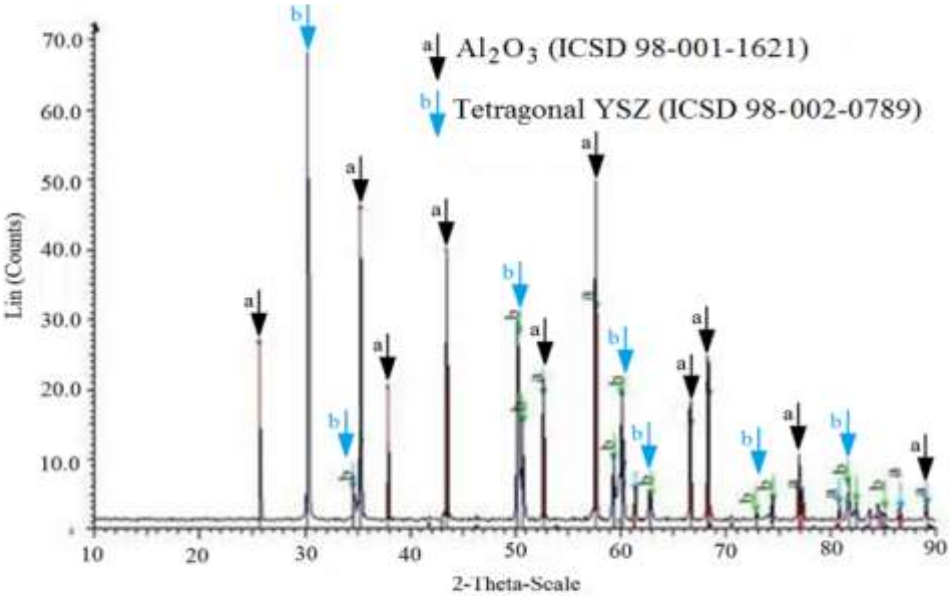

Figure 1 : XRD results of addition of 0.5wt% of Cr_2O_3 into ZTA samples after the sintering process which (a) represent tetragonal alumina corundum (ICSD reference 98-001-1621) and (b) represent the tetragonal yttria stabilized zirconia (ICSD reference 98-002-0789).

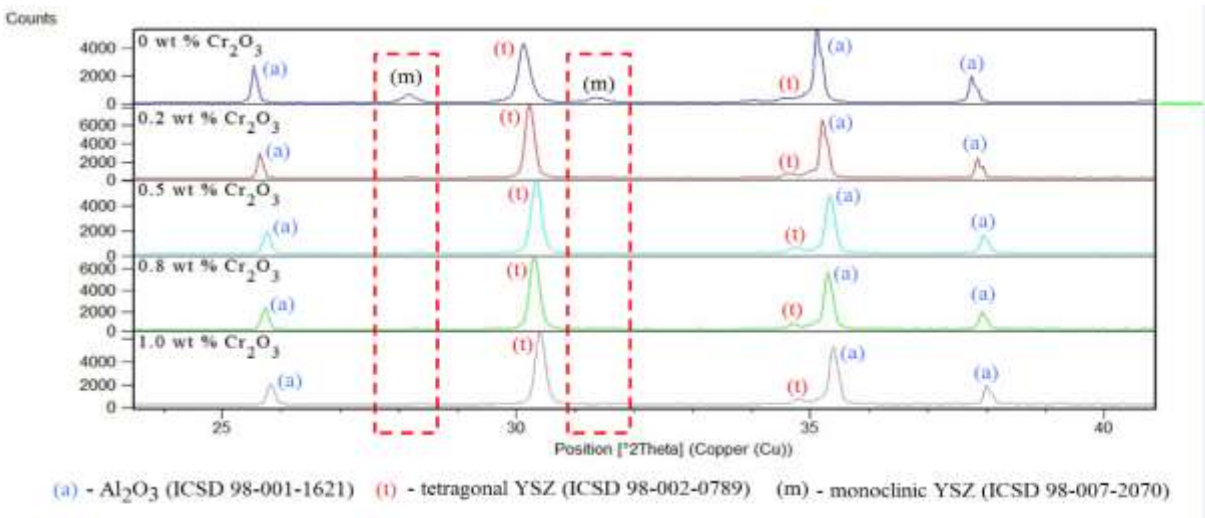

Figure 2: Comparison of XRD results for ZTA samples with various addition of Cr_2O_3 wt%.

Microstructure

FESEM micrographs for the polished surface of the samples are shown in Figure 3. Consistent with previous studies, YSZ and Al_2O_3 grains are well distributed among each other but minor agglomeration was unavoidable (Hao et al., 2010, Smuk et al., 2003). In general, similar microstructural characteristic were observed in these samples i.e. uniformly sized grains with high degree of grain close packing. Almost no abnormal grain growth was observed. Furthermore, few of the dark grains (Al_2O_3) grew with the increase of the Cr_2O_3 wt %. This can be seen from the micrographs by comparing the microstructure with 0 wt% Cr_2O_3 with the microstructure with 1.0 wt% of Cr_2O_3. This proved that Cr_2O_3 had accelerated the growth of alumina grains. A similar observation was recorded in the study of Riu et al., which stated that the average size of grains containing Cr_2O_3 increased compared to the pure ZTA specimen (Riu et al., 2000). In Figure 3(a-b), the presence of Cr_2O_3 grains cannot be seen due to the very low amount of Cr_2O_3 wt% added. However, the presence of Cr^{3-} can be proven based on the EDX results in Figure 3(e). EDX analysis clearly shows the presence of Cr^{3-} in the samples although no grain of Cr_2O_3 is found in the micrograph. When a higher amount of Cr_2O_3 is added, the grains grow and become relatively larger compared to the grains of pure ZTA.

Mechanical Properties

Figure 4 indicates the results of fracture toughness of ZTA-Cr_2O_3 samples with various Cr_2O_3 wt% (Y-error bar indicates the standard deviation value). The samples containing 0.6 wt% Cr_2O_3 showed maximum fracture toughness (5.36 $MPa.m^{1/2}$) compared to other samples. Addition of more Cr_2O_3 than 0.6 wt % would result makes the fracture toughness result to reach a saturated value. The result of fracture toughness increases as much as 15.86 % with the addition of 0.6 Cr_2O_3 wt %.

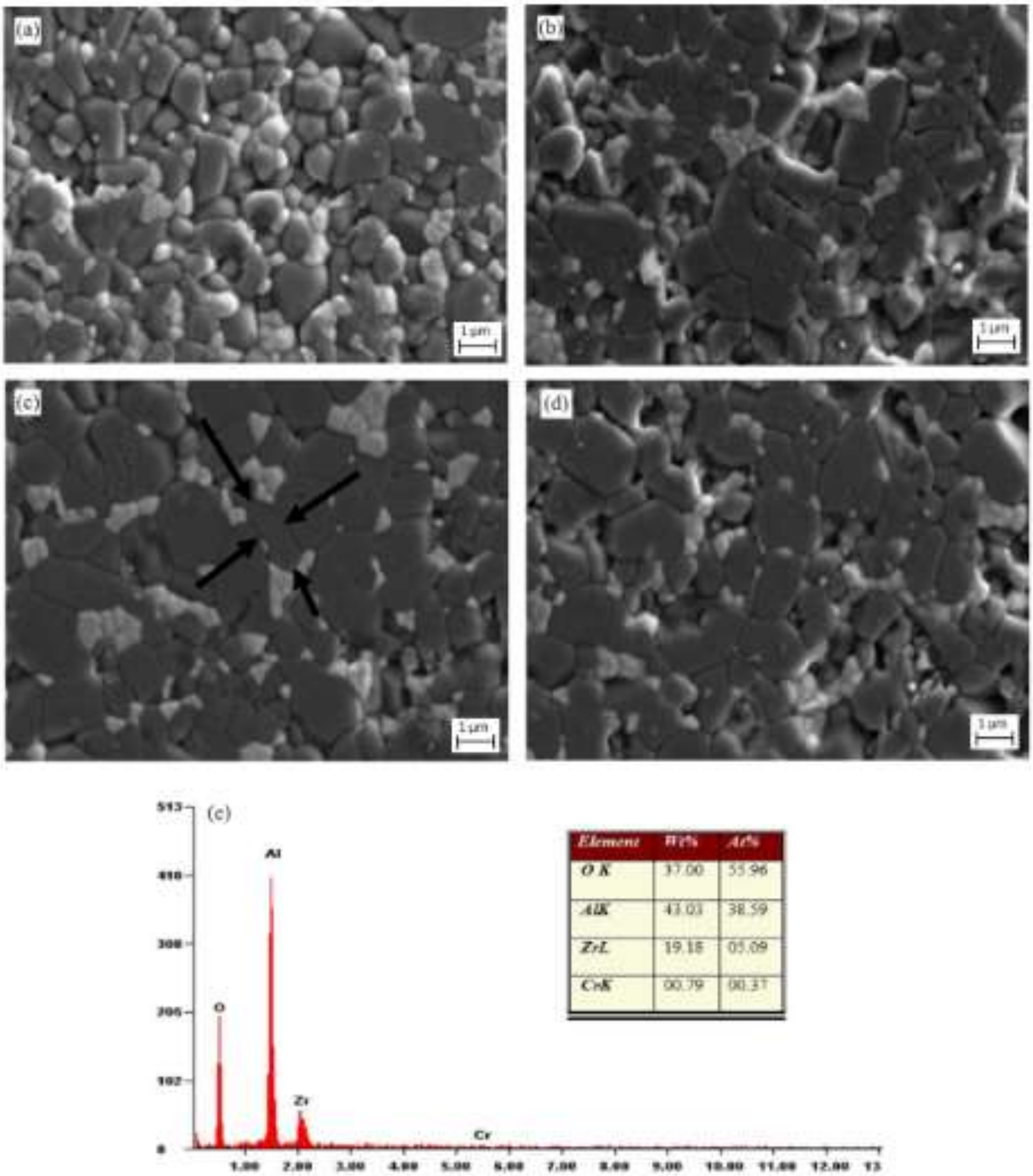

Figure 3: Microstructural images of ZTA-Cr_2O_3 samples with addition of (a) 0 wt% Cr_2O_3, (b) 0.3 wt% Cr_2O_3, (c) 0.6 wt% Cr_2O_3, (d) 0.9 wt% of Cr_2O_3 and (e) EDX results for ZTA-Cr_2O_3 samples which containing 0.8wt% Cr_2O_3. All micrograph were taken with 5000 X magnification.

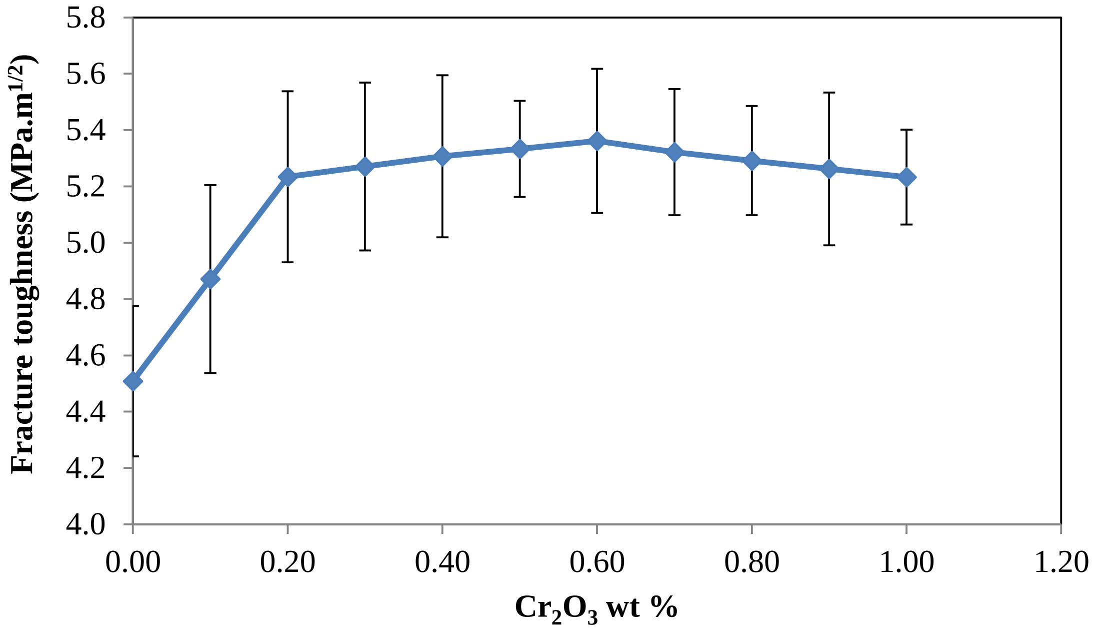

Figure 4: Fracture toughness of ZTA-Cr_2O_3 samples as a function of Cr_2O_3 wt%.

The increase of fracture toughness is mainly caused by the crack bridging due to large grains formed which can be observed in Fig. 4. The previous study conducted by Riu et al. (Riu et al., 2000) concluded that the increase of fracture toughness is due to the formation of large elongated or platelike grains in the microstructure, which can be observed in Fig. 3(c). Large grains formed due to the addition of Cr_2O_3 resulted in higher toughness and provide more resistivity to crack propagation. Addition of 0.7 wt % Cr_2O_3 onwards show decrease of fracture toughness. This is due to the presence of pores inside the sample as a result of vaporization and condensation of Cr_2O_3 in pressureless sintering (Magnani and Brillante, 2005, Hernandez et al., 2003, Hirata et al., 2000). Some authors has also reported similar results (Azhar et al., 2010, Hirata et al., 2000, Maiti and Sil, 2010, Magnani and Brillante, 2005), where as Al_2O_3 with larger grain size would produce higher value of fracture toughness. Work done by Riu et al., (2000) summarizes that the increase of fracture toughness is mainly contributed to the crack bridging by the platelike and larger grains.

CONCLUSION

The effects of Cr_2O_3 addition on the mechanical properties and microstructure of ZTA were investigated. When a small amount of Cr_2O_3 (~0.6 wt %) was added, the grains becomes larger and acquired a platelike shape. As a result, fracture toughness was improved remarkably by the small addition of of Cr_2O_3 (~0.6 wt %).

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