XRD investigation of the Effect of MgO Additives on ZTA-TiO₂ Ceramic Composites

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Abstract. Alumina (Al₂O₃) based ceramics possess good mechanical properties and suitable for the application of cutting inserts. However, this monolithic ceramics suffer from lack of toughness. Hence, there are some modification were made such as the addition of yttria stabilized zirconia (YSZ) to the Al₂O₃ helps in increasing the toughness of the Al₂O₃ ceramics. Some additives such as MgO and TiO₂ were used to further improve the mechanical properties of ZTA. In this study, high purity raw materials which consist of ZTA-TiO₂ were mixed with different amount of MgO (0.0 – 1.0 wt %). The mixture of materials was going through wet mixing, compaction and pressureless sintering at 1600°C for one hour. The samples were characterized for phase analysis, microstructure, shrinkage rate, bulk density, Vickers hardness and fracture toughness. Based on the XRD analysis results, the secondary phase (MgAl₂O₄) was detected in the sample with 0.5 wt% of MgO onwards which leads to grains refinement, thus improve the density and hardness of ZTA-TiO₂-MgO ceramics composites.

1. Introduction
Ceramics, with its excellence physical and mechanical properties, such as low density, strength, hardness and its inertness at high temperature, is widely known as a potential candidate for structural materials with very wide-ranging applications. The ever challenge in dealing with ceramic materials in any engineering application is their low brittleness. It is also having been a massive motivation in the field of ceramics research. In the motivation to enhanced the toughness of ceramic materials, one of the widely known ceramics Al₂O₃ based materials was often used the benchmark due its abundancy, relatively cost efficient, and outstanding mechanical properties.

Secondary component such as yttria-stabilized zirconia can be used to increase toughness of Al₂O₃ based materials. Work done by [1] has explored the effect of Al₂O₃/YSZ ratio to its mechanical and wear performance. His work summarized that 80:20 ratios would give the best wear performance in the turning process. Few authors has also experimented addition of solitary additives into zirconia toughened alumina to increase the toughness; the additives were MgO [2]–[5], Cr₂O₃ [6]–[9], CaCO₃ [10], CeO₂ [11] and TiO₂ [12]–[16]. Addition of MgO has shown to decrease Al₂O₃ grain size, resulting increase hardness and decrease toughness. Cr₂O₃, CaCO₃ and CeO₂ were shown to produce platelike Al₂O₃ grain, increasing to increase toughness and decreasing the hardness. Addition of the mentioned additives also reported to minimize the presence of monoclinic phase in YSZ which could
withheld the t-m phase transformation during the presence of a propagating crack. Due to the additives unique contribution to the Al₂O₃ microstructure, research done by Rejab et al., [4],[17],[18] has focused on using multiple additive into ZTA. His work confirmed the formation of secondary phases which are MgAl₁₋₃CeO₁₉ and MgAl₂O₄ resulted from the addition of MgO into ZTA-CeO₂ ceramic composite. These newly form secondary phase tend to force propagating crack to travel further with crack deflection and crack bridging, resulted in higher fracture toughness.

In this paper, an approach of using two types of additives (3.0 TiO₂ wt % and 0 – 1.0 MgO wt %) was pursued as a continuation of the previous work [14]. This work aims to evaluate the effect of MgO additive on the ZTA-TiO₂ ceramic composite properties with respect to phase analysis.

2. Experimental procedures
The starting raw materials used were Al₂O₃ (Martinswerk, 99% purity), YSZ (Goodfellow, 5.4 mol % Y₂O₃ as stabilizer, 96 % purity), Anatase-TiO₂ (Fluka, Z99%) and MgO (Strem Chemicals, 99% purity). The initial mixture was 80 wt % Al₂O₃ and 20 wt % YSZ and was mixed with different amounts of MgO (0 – 1.0 wt %), whilst maintaining the ratio of Al₂O₃ to YSZ at 4:1. The compositional details are as per table 1. The mixtures were wet mixed using ABB-Mixer Mill with ZrO₂ balls. The slurry was then dried for 24 h at 100 °C in a Memmert-CU9760 oven, following which the dried cake was crushed and passed through a 75 mm sieve. The powders were then hydraulically pressed at 250 MPa for 120 s into pellets of 13 mm diameter and 4 mm thickness without binder. Sintering at 1600 °C for 1h of the pellets were carried out using a Udian furnace model KHT-16000X.

The sintered samples were then analyzed by X-ray diffractometer with CuKα (λ = 1.54056 Å) radiation operating at 40 kV, 40 mA with the 2θ range 10 – 90° and the scanning rate operated at 0.034°/s. The Rietveld refinement method was used to calculate the quantitative amount of each phase.

| Table 1. Compositional details of the experiment. |
| --- | --- | --- | --- |
| Al₂O₃ | YSZ | TiO₂ | MgO |
| wt % | | | |
| 77.60 | 19.40 | 3.00 | 0.00 |
| 77.52 | 19.38 | 3.00 | 0.10 |
| 77.36 | 19.34 | 3.00 | 0.30 |
| 77.20 | 19.30 | 3.00 | 0.50 |
| 77.04 | 19.26 | 3.00 | 0.70 |
| 76.88 | 19.22 | 3.00 | 0.90 |
| 76.80 | 19.20 | 3.00 | 1.00 |

3. Results and Discussion
XRD analysis pattern for ZTA-TiO₂-MgO ceramic composites with varying composition of MgO is shown in figure 1. Three phases were identified in the ZTA-TiO₂ with 0 wt % MgO which are α-Al₂O₃ (ICSD 98-004-0015), t-ZrO₂ (ICSD 98-010-8646), and Zr₀.₃₅TiO₆.₆₅O₂ (ICSD 98-010-4677). The formation of secondary phase of Zr₀.₃₅TiO₆.₆₅O₂ is believed due to the reaction between ZrO and TiO₂ which was no longer incorporated into YSZ grains.

XRD analysis pattern for ZTA-TiO₂-MgO with the addition starting from 0.5 wt% MgO showed the formation of one new phase which is MgAl₂O₄ (ICSD 98-006-1951). This result is parallel to the previous work by Rejab et al. (2014). MgO reacts with Al₂O₃ to form fine secondary phase particles of MgAl₂O₄ due to an excess of MgO above the solubility limit. According to Rejab et al. (2014) the
MgAl₂O₄ peaks were more obvious at the Bragg angle of 37.02°. In this study, the MgAl₂O₄ peaks were seen approximated to angle of 37°. However, the peak only clearly observed in figure 1 at the sample with 1.0 wt% of MgO. Sintering at 1600°C caused the intensity of the corundum phase (α-Al₂O₃) decreased and on the opposite, the spinel phase was found to be increased (Sarkar et al., 1999). The MgAl₂O₄ phase distribution was observed to be increased from 1.5% to 12.6% of phase distribution as shown in table 3.

Phase composition of tetragonal Zirconium Oxide, t-ZrO₂ was decreased from 0.0wt% to 1.0 wt%. The reduction of t-ZrO₂ phase distribution was almost 70%. The reduction is mainly due to the formation of secondary phase which is Zr₀.₃₅Ti₀.₆₅O₂ and the transformations of t-ZrO₂ to m-ZrO₂ phase. According to Chaari et al. (2012), the formation of secondary phase will retard the densification and mechanical properties. Azhar et al. (2014) reported that formation of monoclinic ZrO₂ can be prevented by the addition of stabilizing agent which is TiO₂. Although the amount of TiO₂ was fixed at 3.0 wt%, the formation of monoclinic Zirconium Oxide, m-ZrO₂ (ICDS 98-002-8057) still can be detected when 0.3 wt% of MgO was introduced to the ZTA-TiO₂ ceramics.

Figure 2 shows the enlarged XRD analysis of ZTA-TiO₂-MgO. Peak shifted to a larger angle indicates smaller lattice while broader peak signifies smaller particle sizes.

Figure 1. Normalized XRD analysis in ZTA-TiO₂ ceramic composites with different MgO compositions.
Table 2. Lattice parameter of $\text{Al}_2\text{O}_3$ with different MgO composition.

| MgO wt % | $a$ [Å]   | $c$ [Å]   |
|----------|-----------|-----------|
| 0        | 4.757786  | 12.992480 |
| 0.1      | 4.761736  | 13.003910 |
| 0.3      | 4.768100  | 13.023680 |
| 0.5      | 4.766066  | 13.016570 |
| 0.7      | 4.762318  | 12.999430 |
| 0.9      | 4.763065  | 13.006380 |
| 1.0      | 4.763065  | 13.001860 |

Figure 2. Enlarged XRD analysis in ZTA-$\text{TiO}_2$ ceramic composites with different MgO compositions.
4. Conclusion
The effect of MgO addition on the phases of ZTA- TiO$_2$ ceramics composites was investigated. Addition of 0.5 wt % of MgO onwards only lead to formation of secondary phase, MgAl$_2$O$_4$. The formation of secondary phases is expected to change the physical properties of ZTA. The resulted phase are MgAl$_2$O$_4$. MgO reacts with Al$_2$O$_3$ to form fine secondary phase particles of MgAl$_2$O$_4$ due to an excess of MgO above the solubility limit.

Acknowledgement
This work was funded by the International Islamic University Malaysia (IIUM) under Grant RAGS13-021-0084 and Grant FRGS14-164-0405.

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