

Mechanical behavior of mullite-zirconia composites

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Abstract In this work, mechanical properties of mullite–zirconia composites synthesised through reaction sintering of Algerian kaolin, α -Al₂O₃, and ZrO₂ were characterized. Phases present and their transformations were characterized using x-ray diffraction. Hardness H and fracture toughness K_{IC} were measured by Vickers indentation using a Zwick microhardness tester. The flexural strength was measured through three point bending test using an Instron Universal Testing Machine. It was found that the increase of ZrO₂ content (from 0 to 32wt.%) decreased the microhardness of the composites from 14 to 10.8 GPa. However, the increase of ZrO₂ content (from 0 to 24wt.%) increased the flexural strength of the composites from 142 to 390 MPa then decreased it with further increase of ZrO₂ content. Also, the fracture toughness increased from 1.8 to 2.9 MPa.m^{1/2} with the increase of ZrO₂ content from 0 to 32 wt.%; and the rate of the increase decreased at higher fractions of ZrO₂ content. The average linear coefficient of thermal expansion (within the range 50 to 1450°C) for samples containing 0 and 16 wt.% ZrO₂ sintered at 1600°C for 2 hours was $4.7 \times 10^{-6} \text{ K}^{-1}$ and $5.2 \times 10^{-6} \text{ K}^{-1}$ respectively.

Introduction

Amongst structural engineering materials, mullite ceramics have many desirable properties, such as excellent high-temperature strength and creep resistance, good thermal and chemical stability, low thermal expansion coefficient, and low density [1, 2]. However, monolithic mullite suffers from low values of bending strength and fracture toughness [3]. Zirconia has superior physical and mechanical properties including high hardness, wear resistance, elastic modulus, and high melting temperature [4]; and significant toughening can be obtained by incorporating zirconia particles in a mullite matrix. Different mechanisms are involved in the toughening: stress-induced transformation, microcracking, crack bowing and crack deflection.

Conventional indentation techniques are widely used for mechanical characterization of brittle materials. The advantages of the indentation method include the small size of the test specimen, the easy specimen preparation and the simplicity of the test [5, 6]. It is possible to measure the hardness (H) of the material from the residual impression. Also, analysis of the cracks emerging from the corners of the impression provides quantitative information on fracture toughness (K_{IC}) [5, 7].

Many studies were devoted to the preparation and characterization of mullite-zirconia composites [8-12]. Garrido and co-workers [5] investigated the variation of the H and K_{IC} mechanical parameters as a function of the microstructures of mullite–zirconia composites reaction-sintered from alumina–zircon mixtures from 1450 to 1600 °C under different firing conditions. They found that materials mainly composed by alumina–mullite–zirconia exhibited high hardness and fracture

toughness. Rendtorff and co-workers [13] prepared mullite–zirconia–zircon composites from binary mixtures of zircon and mullite–zirconia powders and measured their mechanical and fracture properties. They concluded that while the flexural strength was related to the microstructure configuration, the other properties such as the young's modulus E , fracture toughness K_{IC} presented clear linear correlation with the composites' composition. They reported that the elastic modulus decreased with the increase of the proportion of mullite–zirconia; and the composites with higher amounts of zirconia had higher fracture toughness. Khor et al [14] prepared mullite-zirconia composites at a relatively low sintering temperature by reaction sintering of plasma spheroidized (PS) zircon-alumina powders in spark plasma sintering (SPS) system. They concluded that with optimized sintering parameters, the combination of PS and SPS was an effective material-processing route for preparing mullite/ZrO₂ composites with attractive mechanical properties from zircon/alumina mixture at a relatively low reaction sintering temperature.

In previous works we synthesised mullite through reaction sintering of Algerian kaolin and Al₂O₃ [14], and investigated the kinetics of mullite formation from Algerian kaolin [15]. Also, we investigated the effect of MgO [16] and ZrO₂ [17] additions on the structure and sintering behaviour of mullite and mullite-zirconia composites. The objective of the present work is to investigate the mechanical behaviour of mullite–zirconia composites synthesised through reaction sintering of Algerian kaolin, α -Al₂O₃, and ZrO₂.

Materials and Experimental Procedures

Raw kaolin (DD3, from Guelma, Algeria) was used in this investigation, its chemical composition as determined by XRF is reported elsewhere [14-15]. α -Al₂O₃ powder (MARTOXTD MDS-6) and zirconia containing 3 mol% Y₂O₃ (3Y-TZP, CRIGERAM) were added to kaolin to obtain 100/00, 92/08, 84/16, 76/24 and 68/32 mullite/ZrO₂ composites (by wt. %), they are named KA00Z, KA08Z, KA16Z, KA24Z and KA32Z respectively. The powders were charged into cylindrical zirconia vials (250 ml in volume) together with 15 zirconia balls (10mm in diameter). Water was added to the mixture at a ratio of 2:1. Ammonium polymethacrylate (1 wt%) was used as dispersant. Ammoniac was added to adjust the pH of the suspension at approximately 10.5. The ball-milling experiments were performed in a high-energy planetary ball mill (Fritsch P6) and were carried out at room temperature at a rotation speed of 250 rpm. The mixture was ball milled for 5 hours followed by attrition for 1 hour using ZrO₂ balls (diameter of 1.2 mm) at a speed of 1250 rpm. After attrition, the slurry was dried at 110°C and subsequently granulated by sieving. Samples containing 08, 16, 24, 32 wt. % ZrO₂ were prepared. A cold uniaxial press was used to shape bars (25x5x2 mm) and discs of 8 mm diameter and compact them at 75 MPa. The green samples were sintered between 1100°C and 1600°C for 2 hours, a heating rate of 10°C /min was used. Phases present and their transformations were characterized using a Bruker x-ray diffractometer model D8 (Cu K α radiation and a Ni-filter) operated at 40 kV, 40 mA with a scanning speed of 0.3°/min and a step of 0.05. Dynamic sintering of the samples was performed using a SETARAM Labsys thermal analyser. The shrinkage versus temperature was measured at a constant heating rate of 10°C/min. Vickers microhardness was measured using a Zwick microhardness tester model 3210; a load of 1000 g was used. The hardness of the samples was quantified using $H_V = 1.8544P/d^2$. The flexural strength of the samples was measured using the three point bending test in an Instron Universal Testing Machine, model 5500R. Experiments were carried out at a cross head speed of 0.5 mm/min using bars having dimension 25x5x2 mm (LxWxH). Fracture toughness was determined using the indentation micro-crack method ($K_{IC} = 0.0937(H_V P/4L)^{1/2}$).

Results and Discussion

The microstructure of samples sintered for 2 hours at 1600°C was composed of mullite grains and ZrO₂ particles. In samples with low ZrO₂ content, mullite grains had whiskers' shape; however, the increase of ZrO₂ content changed the morphology of mullite grains to near spherical shape. ZrO₂

particles were uniformly distributed in the samples. More details on the microstructure and sintering behavior of the prepared mullite-zirconia composites were reported elsewhere [18]. The hardness, fracture toughness and flexural strength of the composites as a function of zirconia content is shown in figure 1. Vicker's hardness of the samples was measured using a load of 1000 g which was optimized using different loads ranging from 100 g to 2000 g. It was found that with the increase of the load, the hardness decreased and remained almost unchanged at loads greater than 800 g. The value of the hardness of each sample was the average of at least six measurements. Even though the samples were carefully prepared, the standard deviation was around 10%. The increase of zirconia content from 0 to 32 wt.% decreased the hardness from 14 to 10.8 GPa respectively as shown in figure 1(a).

Figure 1(b) shows the flexural strength of the samples as a function of ZrO_2 content. The increase of ZrO_2 content from 0 to 24wt.% increased the flexural strength from 142 to 390 MPa then decreased it with further increase of ZrO_2 content. This is due to the fact that for samples containing less than 24 wt.% ZrO_2 , the increase of ZrO_2 content increases the fraction of ZrO_2 changing from tetragonal to monoclinic as it is shown in figure 2 and explained below. It is known that the change from tetragonal to monoclinic generates microcracks that restrict dislocations' movement when the material is stressed. From the other side, when the fraction of monoclinic phase exceeds a specific value it will negatively affect the flexural strength as a result of the formation of macro-cracks which facilitates dislocations' movement. However, it is believed that at high temperatures the flexural strength will continue to increase with the increase of ZrO_2 content up to 32 wt.% because heating will be accompanied with expansion which acts opposite to the polymorphic change from tetragonal to monoclinic.

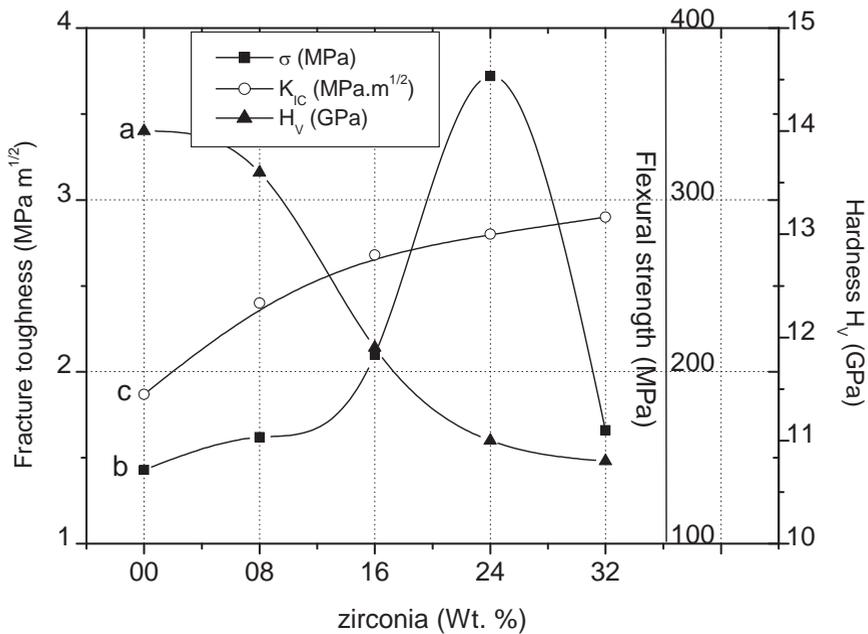


Figure 1: Vicker's hardness, fracture toughness and flexural strength as a function of zirconia content

Figure 1(c) shows the change of fracture toughness as a function of ZrO_2 content. As it clearly seen, the fracture toughness increased from 1.8 to 2.9 $MPa.m^{1/2}$ with the increase of ZrO_2 content from 0 to 32 wt.%; and the rate of the increase decreased at higher fractions of ZrO_2 content.

Quantitative phase analysis was performed following the Rietveld method using the software package X'Pert Highscore Plus. The retained tetragonal fraction of ZrO_2 was obtained from the ratio of intensity of the (111) tetragonal peak to the sum of the intensities of the (111) and $(\bar{1}\bar{1})$ monoclinic and (111) tetragonal peaks [19]. Analysis of qualitative and quantitative XRD data showed that the monoclinic ZrO_2 starts to form at 1400°C and the fraction increased with the increase of temperature up to 1600°C. In the composite containing 16 wt. % ZrO_2 , the ratio of tetragonal zirconia transformed to monoclinic zirconia is relatively small and did not exceed 18%. This ratio has an important role in the improvement of the flexural strength and fracture toughness as discussed above. However, in the composite containing 32 wt. % ZrO_2 around 75 % of the tetragonal structure changed to monoclinic structure which is enough to generate macro-cracks that negatively affect the mechanical performance of the material.

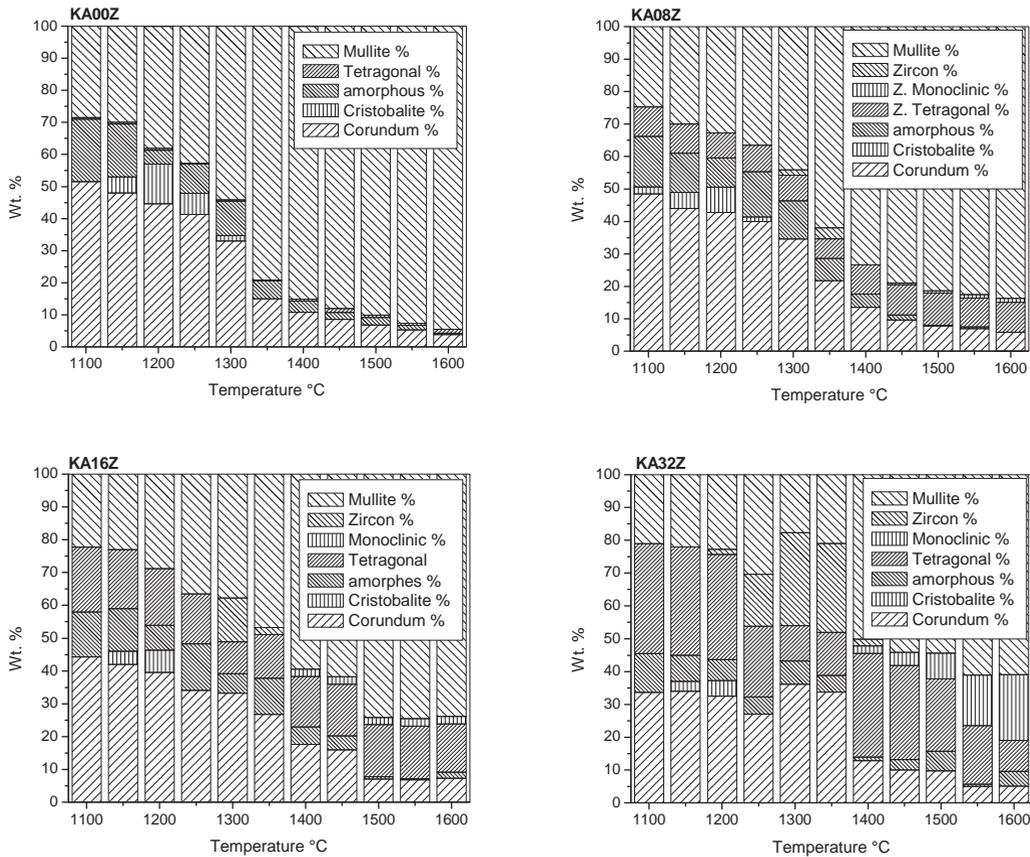


Figure 2: Weight fraction of crystalline and non-crystalline phases present in samples containing 0, 8, 16, and 32 % of ZrO_2 sintered at different temperatures for 2 hours.

The linear coefficient of thermal expansion (within the range 50 to 1450°C) for samples containing 0, 16 and 32 wt.% ZrO_2 sintered at 1600°C for 2 hours is shown in figure 3. The average of the linear coefficient of thermal expansion was $4.7 \times 10^{-6} K^{-1}$ for sample containing 0 wt.% ZrO_2 and $5.2 \times 10^{-6} K^{-1}$ for sample containing 16 wt.% ZrO_2 . This is a good result compared to published works where the average of the linear coefficient of thermal expansion for the same temperature range was between $4.5 \times 10^{-6} K^{-1}$ and $6.3 \times 10^{-6} K^{-1}$ for unreinforced mullite [20,21] and $5.2 \times 10^{-6} K^{-1}$ and $7.2 \times 10^{-6} K^{-1}$ for mullite reinforced with ZrO_2 [22]. For zirconia content higher than 16 wt.% during

heating zirconia will change from monoclinic to tetragonal and the inverse is true during cooling; figure 3 shows that the temperature of change is 480°C for cooling and 920°C for heating. The coefficient of thermal expansion is very important for applications at high temperatures because the lower the coefficient, the longer life time of the material. Pure mullite has very low linear coefficient of thermal expansion, but compared to other materials when it is applied under compressive stress its resistance decreases with the increase of temperature. Therefore, even the addition of zirconia led to a small increase in the coefficient of thermal expansion the improvement in mechanical properties was significant.

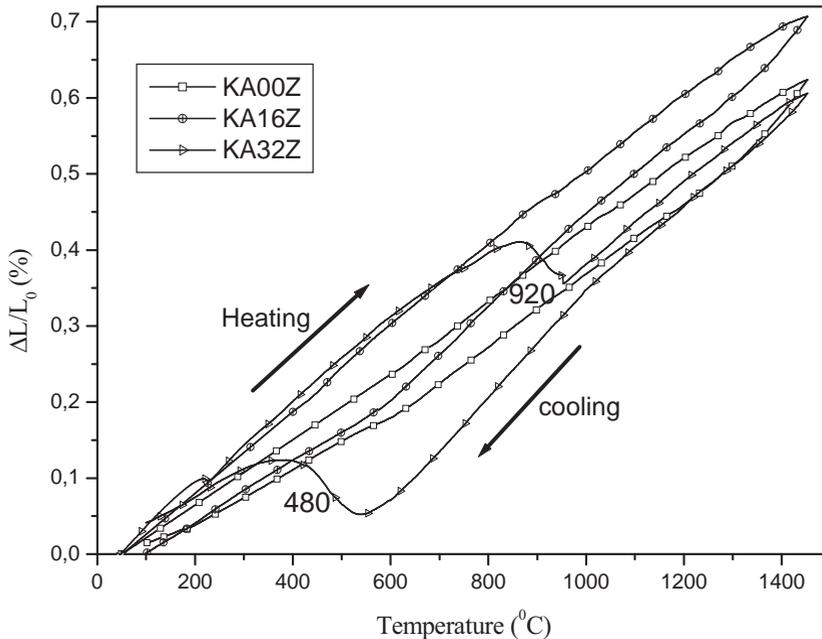


Figure 3: Thermal expansion curves of KA00Z, KA16Z and KA32Z (heating and cooling rate (20°C/min))

Conclusion

Mechanical properties of mullite–zirconia composites synthesised through reaction sintering of Algerian kaolin, α -Al₂O₃, and ZrO₂ were characterized. It was found that the increase of ZrO₂ content (from 0 to 32wt.%) decreased the microhardness of the composites from 14 to 10.8 GPa. However, the increase of ZrO₂ content (from 0 to 24wt.%) increased the flexural strength of the composites from 142 to 390 MPa then decreased it with further increase of ZrO₂ content. The fracture toughness increased from 1.8 to 2.9 MPa.m^{1/2} with the increase of ZrO₂ content from 0 to 32 wt.%; and the rate of the increase decreased at higher fractions of ZrO₂ content. The average linear coefficient of thermal expansion (within the range 50 to 1450°C) for samples containing 0 and 16 wt.% ZrO₂ sintered at 1600°C for 2 hours was between $4.7 \times 10^{-6} \text{ K}^{-1}$ and $5.2 \times 10^{-6} \text{ K}^{-1}$ respectively.

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